PHYSICAL PRINCIPLES AND APPLICATIONS OF MAGNETOCHEMISTRY

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PHYSICAL PRINCIPLES AND APPLICATIONS
OF
MAGNETOCHEMISTRY

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DEDICATED

TO

EDMUND C. STONER

PREFACE

THE numerous investigations which have been conducted all the world over on the subject of Magnetism and Chemistry, particularly on the elucidation of molecular structure and chemical constitution from a knowledge of magnetic properties, have already truly laid the foundations of the subject of magnetochemistry. This subject, owing to its recent origin, is not so well known as the older branches of physical chemistry, such as electro-, photo- and thermo-chemistry. The word 'magnetochemie', the literal English version of which is magnetochemistry, was, however, the title of a German book on the subject published by Professor Wedekind in 1911. The authors have therefore no apologies to offer in selecting the name *Physical Principles and Applications of Magnetochemistry* as the title of this book. As this is the first book in the English language on the chemical side of magnetism or the magnetic side of chemistry, or both, the presentation has of necessity been such as to provide to those who have been introduced to the subject for the first time a readable and easily comprehensible account of the fascinating subject of magnetism and molecular structure, and to furnish investigators in physical chemistry and physics with a more or less complete and up-to-date account of theoretical and experimental researches in this field. We had therefore to retain elementary and somewhat obsolete treatment of certain topics and at the same time to deal with the most recent aspects of those subjects.

That the physicist retains his pagan instinct and worships the rising sun is abundantly clear from the trend of investigations in magnetism and atomic structure since the advent of the New Quantum Mechanics. One by one the physicists are deserting their faith in the orbital atom and seeking for light from this new source. Nor could the writers of this book withstand this temptation. They have attempted, however, to make use of the pictorial representation of the atom side by side with the newer

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A knowledge of the barest outlines of wave-mechanics and spectroscopy is assumed, but in order to make the book complete within the range to which it is restricted, an introduction to spectroscopy and atomic structure has been provided in Chapter V. This may look strange at first sight, but the reader will find that this is the chapter most referred to in the text.

The book is primarily intended for the chemist and the physicist, but it is hoped that it would be of interest also to workers in the allied branches of metallurgy and engineering.

Any merit that this book possesses must be attributed to the writings of the great investigators in the field of magnetism. We are fully conscious of the fact that its defects reflect to a large extent our own shortcomings.

S. S. B.
K. N. M.

THE PANJAB UNIVERSITY, LAHORE
1st July 1933

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It is our pleasant duty to express our thanks and obligation to the numerous workers in the field of magnetism who were kind enough to send us the reprints of their original papers, particularly to Professor G. N. Lewis, Professor Honda and his numerous pupils, Dr. E. C. Stoner, Professor Sir C. V. Raman, Professor K. S. Krishnan, Professor D. M. Bose and Professor P. Ray. We have freely drawn from the following books: Stoner, *Magnetism and Atomic Structure* (Methuen, London, 1926); Stoner, *Magnetism* (Methuen, London, 1930); Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932); Williams, *Magnetic Phenomena* (McGraw - Hill Book Co., New York, 1931); Pauling and Goudsmit, *The Structure of Line Spectra* (McGraw-Hill Book Co., New York, 1930); Wall, *Applied Magnetism* (Benn, London, 1927); L. L. Campbell, *Galvanomagnetic and Thermomagnetic Effects* (Longmans); N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford University Press); G. N. Lewis, *Valence and the Structure of Atoms and Molecules* (Chemical Catalog Co.).

We are indebted to Professor L. W. McKeehan for his article on 'Magnetism in Discontinuous Media' in *Reviews of Modern Physics* (vol. 2, 1930) and to the authors of magnetic theories in the *Bulletin* of the National Research Council (vol. 3, 1922) for much inspiration. We gratefully acknowledge the courtesy of the above authors and of the Editors of the various journals, especially *Journal of the Chemical Society*, *Journal of the American Chemical Society*, *Physical Review*, *Philosophical Transactions of the Royal Society*, *Annalen der Physik*, *Comptes Rendu*, for permission to reproduce figures, diagrams, tables, etc.

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NOTATIONS USED IN THE BOOK

e = Charge of the electron.

m or m_0 = Mass of an electron.

h = Planck's constant.

c = Velocity of light.

k = Boltzmann's constant.

R = Gas constant ($= \mathrm{N}.k$).

N = Avogadro's number.

N_v = Number of molecules for unit volume.

M = Molecular weight.

T = Absolute temperature.

χ = Specific susceptibility (i.e. susceptibility per gm.).

χ_{M} = Gram-molecular susceptibility ($= \chi \times$ Molecular weight).

κ = Susceptibility per unit volume (1 c.c.).

μ = Permanent moment of the molecule (except in Chapter II, where μ denotes magnetic permeability).

μ_{B} or μ_{eff} = 'Effective Bohr magneton number'—defined by the equation $\mu_{\mathrm{eff}} = \sqrt{\dfrac{3k\mathrm{T}\chi_{\mathrm{M}}}{\mathrm{N}\beta^2}} = 2{\cdot}839\sqrt{\chi_{\mathrm{M}}\mathrm{T}}$.

β = Bohr Magneton ($= 4{\cdot}95$ Weiss Magnetons).

p = Weiss Magneton ($p = 14{\cdot}06\sqrt{\mathrm{C_M}}$).

$\mathrm{C_M}$ = Curie's Constant for gm.-molecule.

Spectroscopic Notations

L = Orbital quantum number for the atom.

S = Spin quantum number for the atom.

J = Resultant angular quantum number for the atom.

M = Magnetic quantum number for the atom.

g = Lande splitting factor.

The small letters l, s, j, m, etc., are used instead of the capital letters for denoting values for individual electrons.

Letters with bold faces denote vectors.

Single bars denote true average for a single molecule.

Double bars denote statistical average for a very large number of molecules.

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CHAPTER I

EARLY MAGNETISM

1. HISTORICAL INTRODUCTION

The ancients were acquainted with the fact that lodestone has the power of attracting iron and of communicating this property to iron by contact. As lodestone has been described in the Vedas, the most ancient books of the Hindus, under the name of 'Chumbuk' or the kissing stone, there seems to be hardly any truth in the legend that the discovery of lodestone is due to a Cretan shepherd who was strongly drawn to the earth by his iron-tacked sandals when roaming about in Magnesia, the region in Asia Minor where magnetite is found in abundance. The name 'magnet', however, may have been derived, as Lucretius says, from the rediscovery of this property in magnetite, the iron ore found in Magnesia.

The ancient literature of the Chinese abounds in vague references to the south-pointing chariots, and the Greeks and Romans evidently had also a good deal of empirical and speculative knowledge about magnetic phenomena. The first definite evidence that the lodestone was employed as a land compass dates as far back as the eleventh century, and at the time of the Crusades in the twelfth century its use as a mariner's compass was established by the writings of Neckham of St. Albans.

As is usually the case with the early history of all scientific achievements, the small amount of knowledge available to the ancients was masked by a vast mass of false doctrine built around it. These mysteries surrounding the correct knowledge about the phenomenon were cleared up by the pioneer work of Peter Peregrinus of Maricourt whose identity is revealed to us in the writings of the celebrated Roger Bacon. To Peregrinus goes the credit of introducing the term 'magnetic poles' which he experimentally determined in the case of a ball of lodestone by means of a compass needle as being regions where the magnetic power is most concentrated. To him is also ascribed the discovery that a piece of metal broken asunder from a magnet also behaves like a magnet and that unlike poles attract each other while like poles repel.

After Peter Peregrinus the most outstanding man in this kind of enquiry is William Gilbert of Colchester (1540–1603). The greatest contribution of Gilbert is that he sifted facts from fiction. As he himself was a medical man and a court physician to Queen Elizabeth, he helped much in refuting the superstitions and erroneous conclusions of men of his profession and in differentiating clearly between the magnetic and medicinal properties of the lodestone. Perhaps the two most notable discoveries of Gilbert were: (1) that the earth itself behaves like a magnet, and (2) that iron ceases to be attracted when red hot. He also discovered that substances like paper and cloth do not affect the attractive force of lodestone for iron. Gilbert's *De Magnete* is certainly the first book of interest to investigators in magnetic phenomena.

John Mitchell (1724–1793) and John Robison (1739–1805) conducted the earliest recorded quantitative investigations on magnetism. Mitchell invented the torsion-balance and made the fundamental discovery based upon his and John Robison's observations that 'the attraction and repulsion power of magnets decreases as the squares of the distances from the respective poles increase'.

Mitchell's work was more elaborately tested and verified by Coulomb[1] (1736–1806), but to Poisson[2] belongs the credit of employing the method of mathematical analysis to the elucidation of physico-chemical problems, particularly in the realm of magnetism and electrostatics. As a means for the mathematical derivation of Coulomb's law of the mutual action between magnetic poles Poisson adopted the famous 'two fluid' theory. According to this theory Poisson assumed that all magnetic substances consist of a large number of small magnetic particles containing equal quantities of positive and negative magnetic fluids. These particles themselves conduct the fluids perfectly, but the spaces between them are impenetrable to the fluids, which are, thus, not allowed to pass from one particle to another. In the unmagnetised state the two fluids are united to form the neutral fluid. The process of magnetisation separates the neutral fluid into the two constituents which are displaced in opposite directions.

Poisson showed that the force of repulsion exerted by a quantity, m, of magnetic fluid upon a quantity, m_1, of the same kind placed at a distance, d, from it, is proportional to

$$\frac{mm_1}{d^2}$$

and is independent of the material of which the magnetised body is composed. Poisson also deduced expressions for the magnetic force due to a magnet of any form and also discussed the question of induced magnetism and the forces inside cavities in magnetic bodies. Poisson's treatment is the recognised basis of the modern statistical theory of magnetism, although refinements and extensions of Kelvin and Green have much to do with the success and accuracy of that treatment.

As far as the physical aspect of magnetism is concerned as distinguished from the chemical aspect of the subject, the most outstanding discovery certainly has been the unravelling of the relationship between electricity and magnetism. In 1819 Oersted accidentally discovered at the end of a lecture that a compass needle was deflected when in the neighbourhood of a wire carrying electric current. Oersted[3] communicated the discovery to the French Academy. The subsequent work of Arago, Biot, Savart[4] and Ampère[5] revealed beautifully the mutual magnetic relationship between currents and magnets and currents and currents. In the year 1825 Ampère published an exhaustive memoir on the mathematical theory of electrodynamical phenomena. Bearing the analogy between Poisson's 'two fluid' magnetic element and a solenoid of molecular dimensions in which an electric current is continually flowing, Ampère pictured the process of magnetisation as one which consisted in changing the orientation of these molecular currents either by changing the plane of the current relative to the molecule or by turning the molecules as a whole, so that their axes initially pointing in all directions at random will tend to align themselves parallel to the magnetising field.

Faraday, the Founder of Magnetochemistry.—Faraday was led to his masterly researches in this field by the discoveries of Ampère, Arago and Biot, who showed that an electric current is invariably accompanied by a magnetic field. Faraday wanted to investigate the converse effect. In 1831 he described the famous laws of electromagnetic induction before the Royal Society. The establishment of the reciprocal relationship between magnetism and current electricity afforded further support to the molecular current theory of Ampère as against the 'two fluid' theory of Poisson. It was in the year 1845 that Faraday made the discovery which attracted the attention of chemists to the subject of magnetism. While investigating the rotation of the plane of polarisation of a beam of light traversing a piece of glass placed in a strong magnetic field Faraday noticed that the glass itself possessed magnetic properties opposite to those of iron and other 'magnetic' metals. The case of bismuth, which behaved similarly to glass, had previously been observed by Brugmans. Faraday gave the name 'diamagnetism' to this new phenomenon.

In his usual thorough manner Faraday examined a large number of substances in the solid, liquid and the gaseous state for their magnetic properties and laid the foundation of magnetochemistry by announcing the discovery that all substances whether compounds or elements possessed either the diamagnetic or the magnetic property. The results of these investigations were of far-reaching consequence inasmuch as they opened up a vast field of new research on the subject of the how and why of the magnetic properties of the elements and the compounds. They also had an indirect influence on magnetic theory. According to the 'two fluid' theory of Poisson, the elementary magnets of all substances, when placed in a magnetic field, should be polarised in the same direction. Faraday's observation that the direction of polarisation of diamagnetic bodies is opposite to that of magnetic bodies in a magnetic field turned the scales finally in favour of Ampère's theory of magnetism.

2. SOME IMPORTANT EARLIER THEORIES OF MAGNETISM

Weber's Theory of Magnetism (1854).—Weber[6] developed the hypothesis that the fundamental facts of magnetism may be accounted for on the assumption that the molecules of iron and steel are permanent magnets capable of being turned round their centres. In an unmagnetised piece of iron or steel the molecular magnets are arranged in an irregular manner and they mutually neutralise each other's external field. When this piece is subjected to a magnetising force, some of the molecules are turned so that their magnetic axes lie in the direction of the force. As the intensity of the magnetising force is increased larger and larger number of molecules set themselves in the direction of the force and the piece becomes correspondingly more strongly magnetised until it is 'saturated', which stage corresponds to the arrangements of all molecular magnets in the direction of magnetising force.

Ewing's Theory (1890).—Weber's theory accounts for certain facts of magnetism quite satisfactorily, but there are two important facts which remain unexplained on this view. Firstly, it fails to account for the internal restraint which prevents all molecular magnets being turned into line with the magnetising force, and secondly, it does not explain the phenomenon of residual or 'remanent' magnetism. Ewing's experimental researches on the phenomenon of 'hysteresis' led him to extend the theory of Weber to account for the constraint as being due to the mutual magnetic action between the molecular magnets. Ewing postulated that when a piece of iron is unmagnetised, the molecules are arranged in groups, each group forming a stable magnetic system and producing no external magnetic action. When this group of elements is subjected to a small magnetic field each member of the group becomes somewhat deflected, but the general formation of the group is still maintained. When this force is removed each member of the group returns to its original position and leaves no sign on the external action of the group. This view can be made clearer by examining closely the course of a magnetisation curve (Fig. 1). A glance at this curve shows that at the first stage, o, the magnetic induction is very nearly proportional to the magnetising force and there is no appreciable hysteresis loss at this stage. Moreover, during this stage the rate of increase of magnetic induction with the magnetising force is relatively small. If now the magnetising force is gradually increased, a second stage of magnetisation is reached when the individual components of each group of molecules get more and more deflected until a rupture is caused in some of the groups. The molecules thus broken asunder from the groups rearrange themselves and develop new groups which are more nearly in the direction of the magnetising force.

As the magnetising force is still further increased, it is easily conceivable that more groups are torn asunder in this manner. This stage corresponds to the part of the curve from *a* to *b* and is characterised by a rapid increase in the magnetic induction with the magnetising force. This action goes on until the molecules arrange themselves in their final grouping and a condition of 'saturation' is attained. This stage should correspond to the position when the new groups are all in line with the magnetising force.

These three stages are not sharply distinct from each other, but overlap over a short range. After the attainment of saturation, if the magnetic force is gradually lessened, the magnetisation curve will follow the original curve in so far as the reduction of magnetising force corresponds to a change in the deflection of the individual molecules of a group, but not to rupture of a group. As the magnetising force is still further reduced, the molecular groups begin to break asunder. But owing to the forces between the constituents of the group there is a restraint which hinders the reduction of the magnetism of iron proportionately to the reduction of the magnetising force. The result of this is that, even when the magnetising force is completely removed, there is a considerable amount of residual magnetism still left in the iron corresponding to the point *d* in Fig. 1. Thus the magnetic induction lags behind the magnetis-

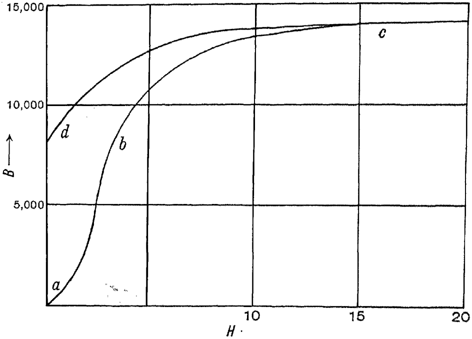


FIG. 1—Magnetisation curve for iron.

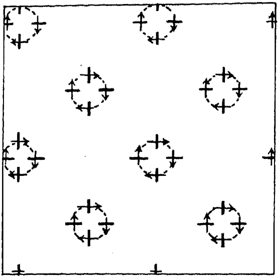
ing force. This phenomenon is known as the 'hysteresis effect'. As Wall puts it, 'If it be assumed that mechanical vibration of the iron results in a greater freedom of movement of the molecules, the fact that such mechanical vibration reduced the amount of remanent magnetism is also accounted for, and similarly the fact that a given magnetising force produces a greater degree of magnetisation in a bar which is being hammered than one which is not so treated. It is easily seen that the effect of hysteresis would lead to a loss of energy dissipated in the form of heat, because each time the individual molecules get separated from a group they are set in vibration and the corresponding kinetic energy is transformed into heat.'

The ideas underlying this theory were beautifully illustrated by Ewing by the construction of a model in which a number of small compass needles were pivoted on a fixed base as representing the constituent molecular magnets in a piece of iron. This model exhibited the phenomena of magnetisation, remanence and hysteresis in a very realistic manner.

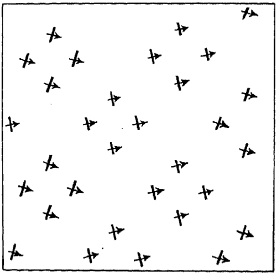
The success of Ewing's theory, particularly as regards the pictorial way in which it made the phenomena of magnetism clear, led him to develop the original form of his theory in accordance with the more modern concepts of the structure of the atom. In his earlier theory, Ewing ascribed the property of elementary magnets to the molecules themselves; but later with the swing in favour of the electronic theory of matter, he changed over to the view that the revolving electrons within the atom give rise to magnetic properties.

A very suggestive experiment was proposed by Swinburne soon after the publication of Ewing's theory. If the theory of Ewing has the kernel of truth in it, then according to Swinburne the hysteresis effect should disappear when a piece of iron is rotated in a very strong magnetic field owing to the molecular magnets being held in line by the magnetising force throughout the cycle, thus preventing the dissipation of energy due to the rupturing of groups of molecular magnets. This prediction has since been verified by Beattie and Clinker.[7]

Evershed's Theory (1920).—Evershed[8] extended the Ampère-Ewing theory of atomic current rings to explain the behaviour of steel, which has a definite crystalline structure. He suggested that, while the current rings are evenly distributed throughout the mass in pure iron, they form, in steel, compact groups separated by relatively large spaces (Fig. 2). Further, in the case of steel the application of a strong magnetising force orientates these 'compact groups' as a whole (Fig. 2A), and not



No Field



Field →

FIGS. 2 and 2A.—Distribution of elementary magnets in steel (Evershed's theory).

the individual current rings only as in pure iron. For further details about Evershed's theory reference should be made to his original paper.

The theories of Ewing and Evershed being pictorial descriptions appeal to those chemists who are not mathematically inclined. The pictorial theories are extremely suggestive but they are at best qualitative, and physical chemistry must look to the more modern theories for satisfaction.

The theories of Langevin, Weiss, Honda, Gans, Oxley and Stoner have cleared the way for a quantitative interpretation of magnetic properties of atoms in terms of electronic structure. These theories will be considered in later chapters, as their significance cannot be comprehended fully unless one is familiar with the units and technique of magnetic measurements and with the magnetic properties of elements. Generally speaking, the chemists neglect these elementary principles of magnetism, as it is erroneously believed by them that this branch of physics has no direct bearing on chemistry. It is with a view to recapitulate the elementary and fundamental concepts of the subject that the next chapter had to be introduced in the book.

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$+m\mathrm{H}$ and the S-pole a force $-m\mathrm{H}$, and since the two are oppositely directed they will give rise to a couple whose turning moment is:

$$\begin{aligned}\text{Couple} &= \text{force} \times \text{arm of the couple}\\ &= m\mathrm{H}\,.\,\mathrm{AN}\ \text{(Fig. 3)}\\ &= m\mathrm{H}\,.\,\mathrm{NS}\times\sin\theta\end{aligned}$$

This couple vanishes when the magnet is parallel to H, i.e. when $\theta = 0$.

When $\theta = 90°$, $\sin\theta = 1$ and the moment equals $m\mathrm{H}\,.\,\mathrm{NS}$. The quantity $m.\mathrm{NS}$, i.e. the pole strength × distance between the poles, is called the *magnetic moment M* of the magnet.

7. MAGNETIC PERMEABILITY

In defining Coulomb's law it was stated that the force between the poles m_1 and m_2 at a distance r cm. apart was given by

$$\mathrm{F} = \frac{m_1 m_2}{r^2}$$

This is strictly true only for vacuo, and is practically the same as for air, but there are many media in which the force between the poles differs considerably from that between the same poles situated in vacuo (or air).

The force equation is, therefore, rewritten in the form

$$\mathrm{F} = \frac{1}{\mu}\,.\,\frac{m_1 m_2}{r^2}$$

where the quantity μ is called the *magnetic permeability* of the medium in which the poles are situated.

It is obvious that μ is equal to unity for vacuo and very nearly unity for air. Also the field due to a pole of strength m at a distance r cm. is $\frac{m}{r^2}$, and this in a medium of permeability μ will become $\mathrm{H} = \frac{m}{\mu r^2}$ or $\mu\mathrm{H} = \frac{m}{r^2}$

8. INTENSITY OF MAGNETISATION

I. The intensity of magnetisation of a magnetised material may be defined as the ratio of the magnetic moment to the volume of any piece of it, the piece being small enough to have uniform magnetisation. Thus,

$$\mathrm{I} = \frac{\text{magnetic moment}}{\text{volume}}$$

II. If a magnetic pole has strength m and an area A sq. cm. at right angles to the direction of magnetisation, then the intensity of magnetisation is

$$I = \frac{m}{A}$$

which defines I as the amount of pole per unit area.

9. MAGNETIC INDUCTION

If a bar of unmagnetised material is placed in a uniform magnetic field the bar becomes magnetised. Inside the material we consider a unit surface in a plane at right angles to the direction of magnetisation. If I be the intensity of magnetisation induced in the material, then from the definition 11 below, there would be $4\pi I$ unit lines of force across the unit area. Also, crossing the unit surface and superimposed on the induced magnetisation is the impressed field of intensity H. Then the total number of unit lines across the unit surface called the magnetic induction is

$$B = 4\pi I + H$$

Also from Gauss' law $B = \mu H$ (see definition 11).

10. MAGNETIC FLUX

The unit of magnetic flux is the 'maxwell'. The total number of lines of force emanating from the face of the north pole of a magnet is called the total magnetic flux, and the number of lines per unit area is termed the flux density.

If through a surface area of A sq. cm. the induction is B, then the flux across the area is given as $B \times A$ maxwells.

11. GAUSS' LAW

The law states that the total normal magnetic induction over a closed surface is 4π times the total amount of pole within it. Mathematically,

$$\int \mu H \,.\, \cos\theta \,.\, ds = 4\pi \Sigma m.$$

The quantity μH is called the magnetic induction B.

If the surface is everywhere normal to the direction of induction, then $\theta = 0$ and $\cos\theta = 1$, or we can say that $4\pi m$ maxwells emanate from a magnetic pole of strength m. The same fact can be expressed differently:

Consider a unit pole situated at the centre of a sphere of radius 1 cm. By definition of field intensity one unit line of force must pass through each sq. cm. of the surface (which is equivalent to saying that the flux through each sq. cm. of surface is one maxwell), and since the surface of the unit sphere is 4π sq. cm., it follows that 4π unit lines emanate from a unit pole.

12. MAGNETIC SUSCEPTIBILITY

Since intensity of magnetisation at any point within a body is proportional to the strength of the field to which it is due, we can write

$$I \propto H \qquad \text{or} \qquad I = \kappa H$$

The factor κ is called the magnetic susceptibility (volume susceptibility) of the material.

Since $B = 4\pi I + H$ (from definition 9)

and also $B = \mu H$ (from definition 11)

we get $\mu H = 4\pi I + H$

and $$I = \frac{\mu - 1}{4\pi} . H = \kappa H$$

which gives $$\kappa = \frac{\mu - 1}{4\pi}$$

or $\mu = 4\pi\kappa + 1$

13. PARA-, DIA- AND FERROMAGNETIC SUBSTANCES

The three classes of substances are distinguished from each other from their behaviour in a magnetic field. Paramagnetic substances when placed in magnetic field get a feeble magnetism induced in the same sense as the external field. There is consequently a greater concentration of lines of force within the body of the substance than in the surrounding field. In a non-uniform field such a substance will experience a tractive force towards the strongest part of the field.

The diamagnetic substances, on the other hand, have a feeble induced magnetising force in the opposite sense to the impressed field. There is therefore a lesser number of lines of force through the substance than in the outside field. The substance, when placed in a non-uniform field, will consequently experience a tractive force towards the weakest part of the field.

The ferromagnetic substances are distinguished by a large value of magnetic permeability and are consequently capable of a high degree of magnetisation. In general these substances are capable of developing N and S poles when placed in a magnetic field.

14. THE PRODUCTION OF MAGNETIC FIELDS

An electromagnet is the most suitable arrangement for producing a magnetic field. Electromagnets of different shapes and forms have been employed according to the nature of the investigation. For example, Du Bois[1] has devised a surgical electromagnet with a straight core increasing in diameter towards the base where it expands into a flange. For eye applications the pole-piece takes the form of a truncated cone, which may have axial boring to accommodate a small glow lamp. The best form of pole-pieces for attracting saturated or unsaturated particles and for eye-applications requires a semi-vertical cone angle of 40°. The weight of an eye-magnet is nearly 50 kilogrammes, while for abdominal applications larger magnets with concave pole-pieces suited to the surface of the body and weighing approximately 100 kilogrammes are employed.

A typical form of magnet employed in physico-chemical investigations consists of two parallel vertical cores secured at their lower ends to a heavy iron base. The coils are wound on bobbins which are slipped over the cores and are so connected that the current flows in opposite direction round them. On the upper ends of the core pole-pieces of suitable shape are provided so that an intense field can be obtained in a suitable narrow gap.

In physico-chemical work, electromagnets producing intense magnetic fields are generally required. For the production of strong fields the following, besides other things, constitute the necessary requisites:

(*a*) A highly permeable material for the core.
(*b*) Suitable shape and size of the cone and the core.
(*c*) A large number of wire turns on the cores.
(*d*) Heavy electric current.

A suitable combination of these requisites leads to the desired type of a magnet for any particular purpose. Thus, Tapp[2] has shown that in magnets which are considerably employed for lifting purposes and for the separation of magnetic ores in metallurgical operations the greatest lifting power, for a given total weight of the material of which the magnet is composed, is attained when the induction in the core corresponds to about 17,000 to 18,000 lines per sq. cm. The area of the pole-pieces according to the same author should not be smaller than that of the core section. If there is to be a considerable non-magnetic gap between the poles, Tapp advises that the pole-pieces should be of even greater area than the section of the core. The question of size in a lifting magnet is also of considerable importance. The ratio of the lifting force of a magnet to its weight is inversely proportional to the dimensions. Smaller magnets have thus a higher 'load ratio' than larger ones. S. P. Thompson has described a small magnet weighing a grain and a half which could lift 2500 times its own weight.

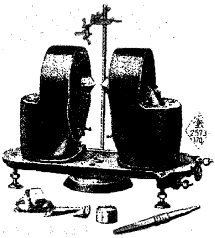

FIG. 4.—Hartmann and Braun's Electromagnet.

H. du Bois and P. Weiss have devoted a good deal of attention to rationalise the construction of electromagnets capable of producing intense fields. In 1891 Du Bois constructed a ring electromagnet capable of giving a field of 40,000 gauss in a gap 1 mm. wide and 6 mm. in diameter. The core of the magnet was made from soft Swedish iron. By using highly permeable alloys higher fields have been obtained.

P. Weiss tried the iron-cobalt alloy Fe_2Co for the pole-pieces, and Du Bois in his famous electromagnets of half-ring type which are in use in many laboratories used for the cores 'Stalloy', which is an alloy of iron with 3 to 4 per cent. of silicon and 0·1 per cent. carbon.

A photograph of this apparatus together with a variety of pole-pieces which are supplied with it by Messrs. Hartmann and Braun is shown in Fig. 4.

The specifications of this magnet as taken from Hartmann and Braun's green list are shown in the following table:

Specifications of the Du Bois Magnet	Large-size Magnet
Maximum strength of field, with pole surfaces 3·6 mm. dia. and 0·5 mm. apart . . . . . (kilogauss)	50 (55?)
Maximum strength of field, with pole surfaces 6 mm. dia. and 1 mm. apart . . . . . (kilogauss)	45 (50?)
Length of the bore hole for optical work in each limb (mm.)	160
Total turns on each limb	1550
Total resistance of each limb . . (ohms approx.)	2·5
Maximum working current admissible for shorter period only . . . . (amperes)	42
Permanent working current, to be checked from time to time . . . . (amperes)	27·5
Diameter of face of limbs (=diameter of the abutment of pole shoes) . . . . . . (mm.)	93
Height from table to pole centre . . . ,,	470
Height from base-plate to pole centre . . ,,	330
Maximum gap between limbs, without pole fittings ,,	260
Length of base-plate . . . . . . ,,	850
Width of base-plate . . . . . . ,,	280
Height from table to top of base-plate . . ,,	140
Height overall . . . . ,,	650
Total weight . . . . . . (kg. approx.)	370

A still larger model of the same type, weighing 1400 kilogrammes and having a pole base of 20 cm., gives in the 0·5 × 3 mm. gap (with ferro-cobalt pole-tips) 65,000 gauss.

Powerful electromagnets have also been recently designed by Weiss, who has adhered to the Ruhmkorff pattern of magnetic circuit having two horizontal coaxial cores supported by a massive yoke, on the ground that coil windings near the air-gap are more effective than those on other parts of the circuit. Weiss recommends, with a view to further improvement in the saturation of the pole-pieces, that the cross-section of the iron should gradually diminish from the distant parts towards the gap, and emphasises the importance of adequate arrangements for cooling the exciting coils.

The effect of change of dimensions of an electromagnet on the field which it produces is governed by the principle of similarity as stated by Kelvin, viz. electromagnets of geometrically similar form give equal magnetic fields at corresponding points if their currents are proportional to their linear dimensions. In similar systems, however, the area of the cross-section of the wire, and therefore its current-carrying capacity, is proportional to the square of the linear dimensions. A small electromagnet would thus require more windings to produce the same field at corresponding points than a large one, otherwise the current would cause excessive heating. It follows also that any further considerable increase of the field in a gap of given dimensions, produced by increasing the size of an electromagnet of the usual type (the field of which is mainly due to the magnetism of the pole-pieces), could only be attained with an exceedingly great increase in the weight, since the weight increases as the cube, while the field at the most increases as the logarithm of the linear dimensions.

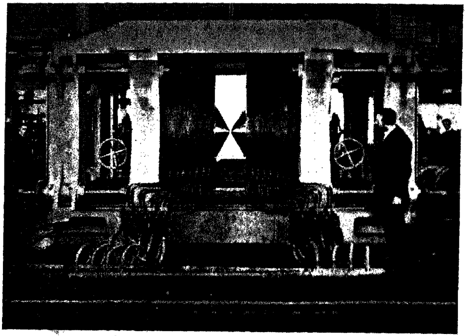

FIG. 5.—Le Grand Électro-Aimant (Cotton Magnet) de l'Académie des Sciences.

15. THE COTTON ELECTROMAGNET

In order to push the Weiss method of obtaining strong magnetic fields to the practical limit, Prof. Cotton (1914), at Paris, proposed to construct an electromagnet giving fields of higher intensity which could be employed in various researches of modern physics, particularly those in magneto-optics. The Great War, however, put an end to these activities, and it was not before November 1922 that the Academie des Sciences under the Presidentship of Marshal Foch decided to construct the electromagnet under review.

It is proposed to give here a brief description of the various parts which will give an idea of the utility of the instrument.

Magnetic Parts.—The electromagnet has a symmetrical form. There are four horizontal girders which form a sort of cage. The horizontal bars are made of soft steel and are fixed together through space which ends in a slit. Under the two smaller girders there are two vertical bearings which carry the core on which the coils slide.

The cores are made of extra-soft steel and are triconic in shape. The axis of the core is traversed by three concentric tubes which are manœuvred by a handle. They terminate at the concentric pole-pieces made of ferro-cobalt and having diameters of 250 mm. and 60 mm. respectively. For a given air-gap the most intense and uniform field is obtained by regulating the pole-pieces with respect to a principal cone. This is accomplished by the aid of the above-mentioned concentric tubes.

Mechanical Parts.—There are four screws which govern the movement of each bearing. The screws are designed to withstand a magnetic repulsion corresponding to 100 tons approximately. They are worked by two electric motors. The path is limited to prevent all accidents which might result when the motors are switched on.

Electrical Parts.—The coils are rolled on cases of bronze, the faces of which are made of aluminium, and which contain tubes of copper in which water circulates, each tube being of 1·55 sq. cm. section. The insulating material comprises 1800 kilometres of paper, 35 kilometres of cotton and 46 kilometres of mica. This can resist an electrical pressure of 10,000 volts. The current employed is 400 amps. at 240 volts, so that the power input is about 100 kilowatts. The number of ampere-turns is equal to $1250 \times 400 = 500,000$.

Magnetic Field.—The maximum field obtained between the pole-pieces is above 53,000 gauss, which accidentally exceeds the calculated value. Higher fields than this (up to 100,000 gauss) can be obtained by placing a supplementary coil in the air-gap. The choice of the coil depends upon the nature of the experiment. The final coils have not yet been constructed, but preliminary experiments on the use of such coils have been promising. The chief interest of this giant electromagnet lies in the fact that it can produce a field of great intensity through a much larger volume than hitherto possible with smaller magnets. There is no doubt that this electromagnet will prove very useful in experiments where steady fields of high intensity are required through large volumes, such as in work on magnetic birefringence.

From experience of the magnetic work done in the Cavendish Laboratory on high intensity fields Lord Rutherford has come to the conclusion that for producing higher intensities the use of iron-cored electromagnets must be abandoned and replaced by the arrangement suggested by Kapitza and others.

16. DESLANDRES AND PEROT'S WORK

In an electromagnet, other conditions being identical, the strength of the field depends upon the magnetism of the iron or the alloy employed and on the current. Deslandres and Perot[3] tried to increase the field by increasing the current as distinguished from the methods adopted by Weiss and Du Bois. Employing a current of 5000 amperes in a water-cooled spiral of bare silver ribbon even without the use of an iron core, a field of 49,900 gauss was obtained. When an iron core was introduced a field of 63,700 gauss was easily obtained. The energy consumption in the coil was at the rate of 340 kilowatts, and the only drawback in these electromagnets was the cost involved.

17. KAPITZA AND WALL'S RESEARCHES

Kapitza[4] described a method of producing intense magnetic fields by means of the discharge of accumulators which send a very strong current through a coil for a very short interval of time.

It is well known that momentary currents of great intensity can be produced by the discharge of a large high-voltage condenser through a coil. Experiments of this kind have been made by Wall[5] in which the duration of discharge was of the order of one-thousandth of a second. It is estimated that in this way a field of about 200,000 gauss may be reached.

The condensers used in the first tests by Wall were paper-insulated, oil-immersed, power type. These condensers were supplied in units of a nominal value of 50 microfarads each, and each unit was capable of standing a charging pressure of 2000 volts d.c.

The condensers were charged by means of a small 20-watt generator in series with a high-voltage battery. The total d.c. pressure available was approximately 2200 volts. The condensers required several minutes to acquire full charge. They could then be suddenly discharged through the solenoidal winding. The solenoid may be compared to the windings of an electromagnet with no iron cores. The winding is immersed in oil, which serves many useful purposes, e.g. (i) it maintains good insulation between neighbouring turns of the solenoid; (ii) it keeps the winding cool, and (iii) it acts as a buffer to the enormous mechanical forces developed between neighbouring turns of the solenoid when the very heavy discharge currents flow in the winding.

18. Kapitza's Later Achievements

Kapitza[6] later achieved even greater success by using a generator of special design which could give a current of about 70,000 amperes at 2000 volts when short-circuited. This heavy current is passed through a specially constructed coil which is strong enough to withstand the tremendous disruptive forces which are produced when such a large current is passed through it. By very ingenious and skilful designing Kapitza has succeeded in generating a magnetic field of 320,000 gauss over a volume of about 3 c.c. without any damage to the coil. It would be possible to increase this field to 500,000 gauss.

Investigations on these intense magnetic fields have been carried out in the Cavendish Laboratory at Cambridge under the inspiring guidance of Lord Rutherford. A highly specialised technique has been developed there for the measurement of currents lasting for about one-hundredth of a second, and oscillographic methods have been employed to determine the strength of the current and the magnetic field. The application of these intense magnetic fields has opened up an entirely new and virgin field of magnetic research.

19. Measurement of Magnetic Fields

Most magnetic balances for susceptibility determinations can be employed for measurements of magnetic fields by using a substance of known susceptibility as the standard. Du Bois,[7] for example, used a modified Quincke method in which the sensitivity was increased by having the narrow tube inclined at a suitable angle θ. The strength of field was calculated from the formula $H = \sqrt{\frac{2g\rho}{\ }}\sqrt{\Delta h \sin\theta}$. (Cf. Chapter III.)

20. THE BISMUTH SPIRAL METHOD

A method which is considerably employed, and which has been made convenient by the manufacture of suitable coils of bismuth by the firm of Hartmann and Braun, is based upon the principle that the specific resistance of bismuth is changed under the influence of a magnetic field. This method is particularly useful for mapping out fields of force round specially constructed magnets and for making 'topographic' surveys. For practical purposes, Lenard spiral is generally chosen. It consists of a small flat, mica-protected, bifilar-wound disc of bismuth wire with flat copper connecting ends, held suitably insulated in an ebonite handle on which the two terminals are mounted. A magnetisation of 1000 gauss increases the resistance by about 5 per cent. The more accurate relationship of field strength to resistance variation is shown in the curve (Fig. 6).

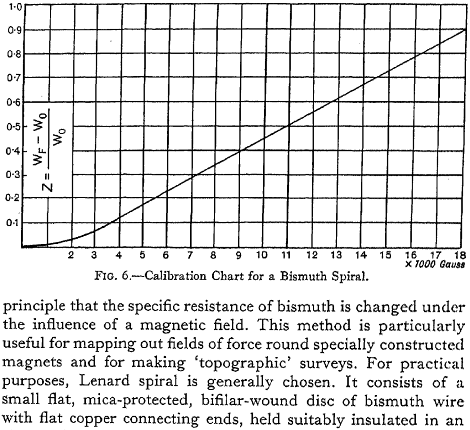

FIG. 6.—Calibration Chart for a Bismuth Spiral.

21. THE FLUXMETER

The most important instrument for measuring field strengths is the Grassot fluxmeter. The principle of this instrument is the same as that of an undamped moving-coil galvanometer. The moving coil is suspended by means of a single silk fibre without any torsion. Thus the control on the moving coil is made negligibly small. A diagrammatic representation of the moving coil system of the Grassot fluxmeter is shown in Fig. 7. The ends of the moving coil are brought out as shown. In order to make the risk of rupture due to mechanical shaking as small as possible, the silk fibre is fixed at the upper end to a flat spiral spring A. The coil is connected through the two spirals CC of thin silver foil. The coil is suspended in the magnetic field of a permanent magnet system NS. For the direct measurements of magnetic flux a search coil is provided which can be connected by terminals to the moving coil of the fluxmeter. If the search coil is made to thread a magnetic flux, or as is usually the case, if the magnetic flux which threads the search coil is altered, it can be shown from the theory that the corresponding deflection of the fluxmeter is directly proportional to the change of flux linkages in the search coil.

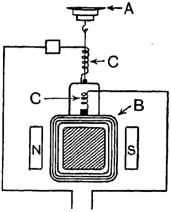

FIG. 7.—Principle of Grassot Fluxmeter.

22. THEORY AND USE OF THE FLUXMETER

A change of the flux in the exploring coil sets up an e.m.f. in the circuit. In consequence a current is generated whose value is $i = \frac{e}{R}$, where R is the resistance of the circuit and e the resultant e.m.f. A couple now acts on the galvanometer coil equal to iAH, where A is the effective area of the coil and H the field strength of the permanent magnet.

If I be the moment of inertia of the moving coil and ω its angular velocity, then

$$iAH = I\frac{d\omega}{dt}$$

where $\frac{d\omega}{dt}$ is the angular acceleration of the coil

or

$$\frac{e}{R}AH = I\frac{d\omega}{dt} \qquad . \quad . \quad . \quad . \quad (i)$$

As e is the resultant of two e.m.f.s, one due to the change of flux $\frac{dN}{dt}$ in the exploring coil and the other AHω due to the rotation of the galvanometer coil with an angular velocity ω, we have

$$e = \frac{dN}{dt} - AH\omega = \frac{dN}{dt} - AH\frac{d\theta}{dt}$$

Substituting for e from equation (i) we get

$$\frac{AH}{R}\left(\frac{dN}{dt} - AH\frac{d\theta}{dt}\right) = I\frac{d\omega}{dt}$$

On integration

$$\frac{AH}{R}\int_0^t\left(\frac{dN}{dt} - AH\frac{d\theta}{dt}\right)dt = I\int_0^t\frac{d\omega}{dt}dt \qquad . \qquad . \quad \text{(ii)}$$

Since the coil is at rest before and after the change in the flux takes place, $\Big[\omega\Big]_{t=0}^{t=t} = 0$, hence both the limiting values of the right-hand side integral are zero.

The left-hand side of equation (ii) gives

$$\int_0^t\left(\frac{dN}{dt} - AH\frac{d\theta}{dt}\right)dt = 0$$

or

$$N = AH\theta = c\theta$$

Thus the relation is independent of the time in which the change of flux takes place.

The Grassot fluxmeter needs a good deal of care in use. Owing to the small clearances in the moving system the levelling of the instrument requires to be carefully done. Small variations in the resistance of the external circuit of the instrument (i.e. the resistance of the search coil and leads) do not affect the readings provided the total external resistance does not exceed the value specified by the manufacturers. The best results are, of course, obtained by keeping the external resistance as low as possible consistent with the necessary number of turns required in the search coil. As the mechanical control in the suspension is very small, the zero of the instrument has a tendency to change a little. This, however, does not affect the readings of the instrument. For testing permanent magnets the throw on the fluxmeter should be noted when the search coil is moved from a position embracing the magnet at its middle point until it is free from the magnet and out of its field. The throw can be doubled if the search coil is taken off and quickly put on again so that the same pole enters the other side of the coil. The rate at which this operation takes place is immaterial within fairly wide limits.

The method of obtaining absolute results of magnetic density can best be illustrated by a numerical example taken for an instrument supplied by the Cambridge Scientific Instrument Co.

The instrument is calibrated so that 1 div. on scale $=15{,}000$ maxwell turns.

Number of turns in the search coil $=34$.

Mean area of one turn $=25$ sq. cm.

Now with the search coil connected to the fluxmeter, 1 scale division has a value of $\frac{15{,}000}{34}$ C.G.S. lines $=441 \cdot 1$ C.G.S. lines, which is the total flux interlinked with the search coil. Hence the density of the flux

$$=\frac{15{,}000}{34 \times \text{area of the coil}}$$

$$=\frac{15{,}000}{34 \times 25}$$

$$=17 \cdot 65 \text{ C.G.S. lines per sq. cm. or gauss.}$$

Hence to find the flux density in the gap of a magnet using the particular search coil the observed deflection is simply multiplied by the above figure.

23. THE MAGNETOMETER METHOD

The magnetometer is one of the simplest and most fundamental pieces of apparatus for measuring magnetic quantities. The form which the instrument takes varies considerably according to the nature of measurement required. The magnetometer may be used to measure (i) intensity of magnetic field, (ii) direction of magnetic field, and (iii) intensity and direction together. An excellent account of the various types of magnetometers employed is given in the *Dictionary of Applied Physics*, vol. ii, edited by Sir Richard Glazebrook, and the reader is referred also to the excellent treatise on *Applied Magnetism* by Wall, published by Ernest Benn Ltd. It is sometimes necessary, particularly in metallurgical investigations and in relation to work on alloys, to test the permeability and magnetic behaviour of ferromagnetic materials in a complete manner. Books on applied physics and engineering deal exhaustively with the various types of instruments in use for this purpose. It will suffice for our purpose to give a brief account of an important laboratory method.

24. THE BALLISTIC METHOD

The material in this method is taken in the form of a ring of circular cross-section. The ring is wound with two sets of coils, (i) the primary in the form of an endless solenoid which carries the magnetising current, and (ii) the secondary wound on the primary, consisting of a number of turns of fine wire. A ballistic galvanometer is connected in series with the secondary.

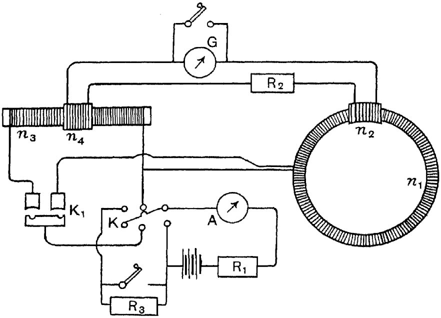

FIG. 8.—Ballistic method for measuring permeability.

If C is the current in the primary as measured by the ammeter A, the magnetising field of the solenoid is given by

$$H = \frac{4\pi n_1 C}{10}$$

where n_1 is the number of primary turns per cm. length. Also, if B is the magnetic induction in the material and α the area of cross-section of the ring, the magnetic flux threading the secondary coil (of n_2 turns per cm.) is given by Bα. The e.m.f. generated by sudden change of this magnetic flux gives rise to a quantity of electricity in the circuit. The charge circulating in the galvanometer is then $\frac{B.\alpha.n_2}{R}$, R being the resistance of the secondary turns. If this produces a throw θ of the galvanometer, then

$$\frac{B.\alpha.n_2}{R}=\kappa\theta$$

where κ is the constant of the galvanometer, which may be determined by means of a standardising solenoidal inductor. Hence we have

$$B=\frac{R.\kappa\theta}{\alpha.n_2}$$

It is more convenient in practice to keep the secondary of the standard inductor permanently in series with the ballistic galvanometer and measure κ by sending a known current C_1 in the primary of the inductor. If n_3 and n_4 are the number of turns per unit length in the primary and secondary, respectively, of the standard inductor and θ_1 be the galvanometer throw produced with current C_1 in the primary of the inductor, then

$$\frac{4\pi n_3 n_4 C_1 A}{10R}=\kappa\theta_1$$

where A = area of the cross-section. R remains the same in both cases, as the two secondaries are permanently in series with the galvanometer. Eliminating κ then gives for B the expression

$$B=\frac{4\pi n_3 n_4 C_1 A}{10\alpha n_2 \theta_1}.\theta$$

and, since $$H=\frac{4\pi n_1 C}{10}$$

it is possible in this way to plot a hysteresis cycle or to determine the permeability of the material.

For testing the magnetic properties of iron in bulk without making it into the form of a wire or ring, Drysdale[8] employed an instrument called the 'permeameter'. A very elaborate type of permeameter has been described by Burrows[9] and extensively used by Yensen[10] for a large number of experiments. For full details of the methods and the corrections required reference must be made to the original papers or to Wall's *Applied Magnetism*.

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EXPERIMENTAL METHODS FOR MEASURING SUSCEPTIBILITY

1. Earlier Work

The most important magnetic measurement from the standpoint of theory is the determination of magnetic susceptibility. Among the earlier methods for the measurement of susceptibilities of strongly diamagnetic substances like bismuth mention may be made of the induction method employed by Von Ettingshausen[1] and others. The method involved the measurement of change in induction through a coil when the substance to be examined was introduced into the core instead of the air. Von Ettingshausen employed two primary coils in series which had secondaries wound round them and which were connected in opposition through a galvanometer. Employing an interrupted current in the primary circuit with a synchronous commutator in the secondary, a balance was obtained. A bismuth cylinder was next inserted in one of the primary coils. This caused a disturbance in the balancing, which was compared by introducing in place of a cylinder of bismuth a solenoid through which a known interrupted current was passed. From the results the permeability of bismuth could be calculated. A somewhat similar method for the determination of susceptibilities of paramagnetic solutions was employed by Townsend. More refined methods have since been developed and the above methods are of historical interest only.

2. General Theory of Susceptibility Measurements

The mechanical forces acting on a body in a magnetic field can be regarded as the superposition of two systems: first, the forces acting on the body in virtue of its permanent magnetism, and secondly, the forces acting on the body in virtue of its induced magnetism.

For the value of F_x, the x-component of the mechanical force per unit volume, Jeans[2] gives the equation in the form

$$F_x = -\rho\frac{\partial\Omega}{\partial x} - \frac{H^2}{8\pi}\frac{\partial\mu}{\partial x} + \frac{\partial}{\partial x}\left(\frac{H^2}{8\pi}\tau\frac{\partial\mu}{\partial\tau}\right) \quad . \quad . \quad (1)$$

where ρ is the density of magnetic poles, Ω is the magnetic potential and τ is the density of the magnetic fluid, μ and H are permeability and field respectively.

Equations similar to (1) can be written for the mechanical force along the y- and z-components.

For a body which has no permanent magnetism the first term of equation (1), $-\rho\frac{\partial\Omega}{\partial x}$, vanishes so that the equation reduces to

$$F_x = -\frac{H^2}{8\pi}.\frac{\partial\mu}{\partial x} + \frac{\partial}{\partial x}\left(\frac{H^2}{8\pi}\tau\frac{\partial\mu}{\partial\tau}\right) . \qquad . \qquad . \qquad (2)$$

It can, further, be shown that, in general, $(\mu - 1)$ is proportional to τ, and consequently we can write

$$(\mu - 1) = c\tau$$

where c is a constant. Also, if the medium is isotropic $\frac{\partial\mu}{\partial x} = 0$, and the equation (2) may be put in the simpler form

$$F_x = \frac{\mu - 1}{8\pi}\frac{\partial}{\partial x}(H^2) \qquad . \qquad . \qquad . \qquad (3)$$

Also, there will be similar equations for the forces along y- and z-axes, i.e.

$$F_y = \frac{\mu - 1}{8\pi}\frac{\partial}{\partial y}(H^2). \qquad . \qquad . \qquad . \qquad (4)$$

and

$$F_z = \frac{\mu - 1}{8\pi}\frac{\partial}{\partial z}(H^2) . \qquad . \qquad . \qquad . \qquad (5)$$

For practical applications the equations (3), (4) and (5) can be further simplified by taking the field along the y-direction, its gradient along the x-direction and supposing the field uniform along y- and z-axes. Consequently, equations (4) and (5) reduce to zero.

If a body having a volume v, with a permeability μ_1, is suspended in a medium of permeability μ_2, we can rewrite the equation (3)

$$F_x = \frac{\mu_1 - \mu_2}{4\pi}vH_y\frac{\partial H_y}{\partial x} \qquad . \qquad . \qquad . \qquad (6)$$

or since $\mu = 1 + 4\pi\kappa$ where κ is the volume susceptibility, we have

$$F_x = (\kappa_1 - \kappa_2)vH_y\frac{\partial H_y}{\partial x} \qquad . \qquad . \qquad . \qquad (7)$$

Further, we can consider the case where the field is uniform, but the body is in the form of a long uniform cylinder with its axis lying, say, along the x-axis so that its one end is in a field of strength H_1 and the other end lies in a region of field H_2. Inside the body there would, then, be a field gradient with $H = H_1$ at $x = 0$ and $H = H_2$ at the other extremity. Consequently we get on integration from equation (3)

$$F_x = \frac{\mu - 1}{8\pi}(H_1^2 - H_2^2)$$

Substituting $\mu = 1 + 4\pi\kappa$ and remembering that equation (3) refers to a unit volume,

$$F_x = \tfrac{1}{2}(\kappa_1 - \kappa_2)AH^2 \quad . \quad . \quad . \quad (8)$$

where A is the area of the cross-section of the cylindrical specimen.

The equations (7) and (8) are of fundamental importance from the point of view of practical susceptibility measurements and all the present methods of measurement depend on one or the other of these.

It is sometimes more convenient to express measurements in terms of specific or mass susceptibility, χ, which is susceptibility per unit mass of the substance. Since κ refers to unit volume, we have

$$\chi = \frac{\kappa}{\rho}$$

where ρ is the density of the substance, since $\rho = \frac{\text{mass}}{\text{volume}}$, we obtain

$$\chi m = \kappa v$$

or substituting for κv in the equation (7) we get for mechanical force in a non-homogeneous field

$$F_x = (\chi_1 m_1 - \chi_2 m_2)H_y \frac{\partial H_y}{\partial x} \quad . \quad . \quad . \quad (9)$$

where χ_1 and χ_2 are the mass susceptibilities of the substance and medium respectively, m_1 is the mass of the specimen taken and m_2 the mass of the medium occupying the same volume as the specimen.

According to the theory developed above, the methods of measurements of magnetic susceptibilities can be broadly classed under two main divisions:

(i) Non-uniform field methods,
(ii) Uniform field methods.

The earliest application of the non-uniform field method to practical susceptibility measurements is due to Faraday[3] and the method is known after him. The uniform field method for solids is known after Gouy[4], although this method was applied for liquids by Quincke[5] in 1885.

3. FARADAY METHOD

Faraday's method[3] for measuring susceptibilities makes use of the force in a non-homogeneous field. The specimen in the form of a cylinder is suspended from one arm of a torsion balance in a suitable non-uniform field, obtained by inclining the two pole-pieces of an electromagnet at a certain angle, as shown in Fig. 9. If v be the volume of the specimen such that the field is uniform over it, the mechanical force, according to equation (7), is

$$F_x = (\kappa_1 - \kappa_2) v H_y \frac{\partial H_y}{\partial x}$$

where κ_1 and κ_2 represent the volume susceptibilities of the material of which the specimen is made and of the medium respectively.

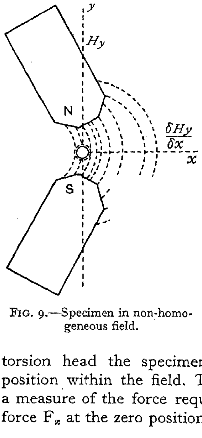

FIG. 9.—Specimen in non-homogeneous field.

The force is directed along the x-axis and gives a displacement to the specimen. By using the torsion head the specimen is brought back to its original position within the field. The twist on the torsion head gives a measure of the force required to just balance the magnetic force F_x at the zero position.

For absolute measurements H and $\frac{\partial H_y}{\partial x}$ have both to be determined experimentally. H can be measured by any of the methods discussed in Chapter II, but for measuring $\frac{\partial H}{\partial x}$ use has to be made of a test coil and a ballistic galvanometer. This is a matter of some difficulty as the gradient may vary from point to point. For this reason also it becomes important that the zero-position of the test specimen should not be allowed to change by any appreciable amount during the course of observations. Consequently deflection methods have to be replaced by torsion-head methods. Faraday himself recorded observations in terms of the change of the torsion-head angle θ. Refinements have been introduced in this method by Curie, Wilson and others. In another arrangement based upon the same principle the deflections are magnified by suspending a mirror from a bifilar suspension, the actual movement of the specimen being almost negligible. A similar but more refined arrangement is made use of in the interference balance. A ballistic method has been recently used by Bhatnagar and K. N. Mathur in which the 'throw' due to a momentary field is measured. These methods have been described in greater detail later.

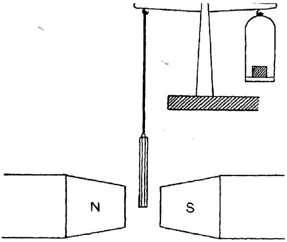

FIG. 10.—Principle of Gouy Balance (homogeneous field).

4. GOUY METHOD

Gouy[4] considers a cylinder suspended in a magnetic field (Fig. 10); one end of the cylinder is in a uniform magnetic field between the poles of the strong magnet N S and the other end is in a region where, the field is negligible. The axis of the cylinder is at right angles to the field. Let A be the cross-sectional area of the cylinder and H the field strength, then the force acting on the cylinder along its axis is, as before,

$$F_x = \frac{1}{2}(\kappa_1 - \kappa_2)H^2A$$

where κ_1 and κ_2 represent the volume susceptibilities of the material of the cylinder and the medium respectively.

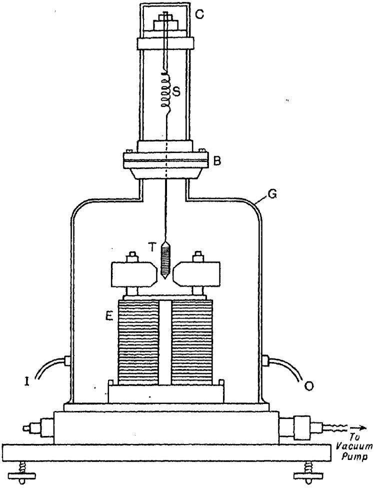

FIG. 11.—A simple Gouy Balance.

S=suspension spiral.
T=tube with specimen.
E=electromagnet.
C=brass cap to make the instrument airtight.
B=brass flange.
G=glass case.
I and O=inlet and outlet tubes for filling instrument with any desired gas.

If the field at the farther end of the cylinder is not zero, it is accounted for by replacing H^2 by $(H_1^2 - H_2^2)$ in the above equation, where H_2 is the small field at the farther end of the specimen.

The force on the specimen can be directly determined by suspending the cylinder from the arm of a sensitive type of balance and finding the change in weight due to the field, or the cylinder may be supported from a horizontal torsion arm and F_x read in terms of torsional angle θ.

The Gouy method constitutes an excellent arrangement for determining the absolute values of susceptibilities as the force in this case is measured in the absolute units. As a uniform field is employed its measurement offers no particular difficulty.

5. A SIMPLE GOUY BALANCE

A useful and easily rigged up magnetic balance of the type of Gouy has been described by Bhatnagar, Mathur and Kapur[6] for determining susceptibilities of feebly para- and diamagnetic substances and is shown in Fig. 11.

The apparatus consists essentially of a fine silver spiral suspended from a stout brass hook at the top of the case. The lower end of the spiral is attached to a piece of light string carrying a fine hook to which a small thin glass tube containing the specimen could be suspended. The lower end of the specimen tube comes between the poles of an electromagnet M. The spring acts as a sensitive Jolly balance. According to the principle of this balance, the force acting is proportional to the pull and, therefore, the vertical displacement when magnetising current is put on measures the force acting on the substance due to the magnetic field. The displacement is accurately measured by means of a measuring microscope provided with a micrometer eyepiece. As in Gouy's method, $F = \frac{1}{2}(\kappa_1 - \kappa_2)AH^2$, but F in this case is equal to Eg/x,

where E = increase in pull in cm. in the field,
x = pull in cm. produced by 1 gm.,
g = gravity constant.

Thus $$\frac{Eg}{x} = \frac{1}{2}(\kappa_1 - \kappa_2)AH^2$$

Since, in conducting measurements by this method, the tube and magnetic field are kept the same throughout, the expression AH^2 in the above equation can be regarded as a constant of the instrument, and when susceptibilities are required in absolute units the constant can be calculated in the following manner:

A substance of known magnetic susceptibility, say water, is taken and the value of E is experimentally determined. Since g, x and κ_1 and κ_2 are known, the value of AH^2 is easily calculable.

6. QUINCKE METHOD FOR LIQUIDS

The underlying principle of this method[5] is the same as that of the Gouy method. Instead of determining the force by direct weighing, the force due to the rise of the liquid in a capillary tube can be calculated from a knowledge of the height to which the liquid rises, the density of the solution and the gravity constant.

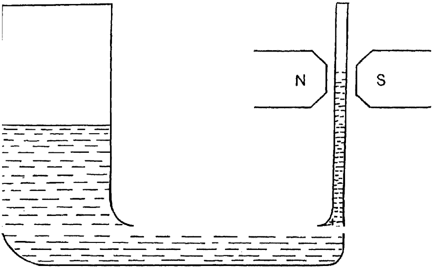

FIG. 12.—Principle of Quincke method for liquids.

A modified U-tube is employed, one limb of which is of a very narrow bore. The narrow tube is placed between the poles of a magnet so that the meniscus of the liquid is in the region where the magnetic field is most uniform. The field near the wider end of the U-tube is negligible. When the field is applied the meniscus rises or falls. If h is the height by which the liquid rises or falls, then the hydrostatic pressure is $p = \rho gh$ where ρ is the density of the liquid. This pressure balances the magnetic force due to the field so that

$$p = \rho gh = \tfrac{1}{2}(\kappa - \kappa_0)H^2 \quad . \quad . \quad . \quad (10)$$

κ being the susceptibility of the liquid and κ_0 the susceptibility of the gas over the meniscus.

From equation (10),

$$\frac{2\rho gh}{H^2} = \kappa - \kappa_0$$

which gives

$$\frac{2gh}{H^2} = \frac{\kappa}{\rho} - \frac{\kappa_0}{\rho_0}\cdot\frac{\rho_0}{\rho}$$

or

$$\kappa = \frac{2gh}{H^2} + \frac{\kappa_0}{\rho_0}\cdot\frac{\rho_0}{\rho}$$

Hence

$$\chi = \frac{2gh}{H^2} + \chi_0\frac{\rho_0}{\rho} \quad . \quad . \quad . \quad . \quad (11)$$

where χ is the mass susceptibility.

For measurements in the case of liquids and gases several ingenious and original arrangements based on Quincke's U-tube method have been described in literature. The form of apparatus as originally designed by Bauer and Piccard [7] for accurate measurements of the susceptibilities of liquids and gases is now universally employed. A diagrammatic sketch of the apparatus is given in Fig. 13.

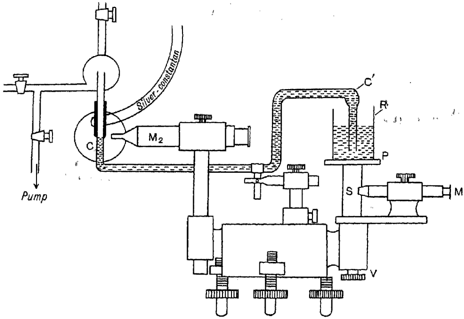

FIG. 13.—Bauer and Piccard Apparatus for susceptibility measurements.

7. BAUER AND PICCARD'S MAGNETIC BALANCE

The apparatus consists essentially of an elaborate tube CC' suitably held in position on a stout stand provided with levelling screws as shown in the figure. The magnetic field is applied at the capillary end C of the U-tube, which is about 3 mm. in diameter. The meniscus is brought back to its original position by the raising or lowering of the reservoir R by means of a micrometric device V. The meniscus was observed through M_2. A straight filament lamp was used for making the settings. The temperature changes could be measured to 0·1° C. by means of a thermocouple of constantan and silver. The change in the height of the reservoir R in order to adjust the level of the meniscus was read off the glass-scale S marked in 1/100 mm. by means of a micrometer eyepiece M_1. For liquids the equations described under Quincke's method are applicable. For testing gases the apparatus was initially tested for water in an atmosphere of hydrogen, as the volume susceptibility of this gas is negligible, being only 0·02 per cent. of that of water. The susceptibility of the gas under investigation was determined by measuring the heights to which the liquid meniscus moved in the two experiments. If h_0 is the change in the level of the meniscus in the first case and h in the second, and if κ_0 is the

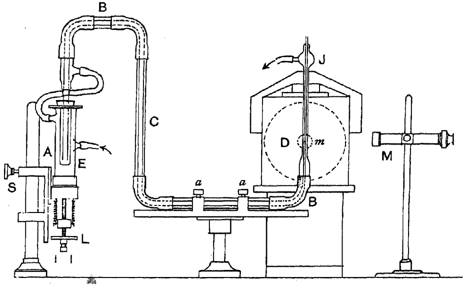

FIG. 14.—Modified Bauer-Piccard Apparatus.

B-B = tube with water-circulating concentric jacket.
J = jacket for water circulation around meniscus.
M = measuring microscope with filar micrometer eyepiece.
m = position of the liquid meniscus within the poles (dotted circle).
A = reservoir with water-circulating outer jacket.
S = stand with raising or lowering adjustment.
L = micrometric adjustment for adjusting the level of the meniscus.
a-*a* = arrangement for clamping the tube in position.

volume susceptibility of water, then κ, the volume susceptibility of the gas under examination, is given by

$$\kappa = \kappa_0 \frac{h - h_0}{h}$$

Bauer and Piccard have described two other methods in which O-tubes have been substituted for the U-tube, and other refinements and improvements have also been introduced for determining the susceptibilities of the gases. The underlying principles of these methods, however, remain the same.

8. SUSCEPTIBILITIES OF SOLUTIONS

The Bauer-Piccard method forms a very convenient method for the investigations of solutions. As in equation (11) the specific susceptibility of the solution can be calculated from

$$\chi_{\text{sol}} = \frac{2gh}{H^2} + \chi_a \frac{\rho_a}{\rho_{\text{sol}}}$$

where χ_a and ρ_a refer to the susceptibility and density respectively of air or any other gas in contact with the meniscus of the solution.

The mass susceptibility of the dissolved material can be calculated from that of the solution by correcting for the susceptibility of water or any other solvent.

If χ_{sol}, χ_s and χ_w be the respective susceptibilities of the solution, the salt and water, then

$$\chi_{\text{sol}} = C_s \chi_s + (1 - C_s) \chi_w$$

where C_s, the concentration of the salt, should be taken to be the weight of the substance dissolved, divided by the total weight of the solution.

The relation does not take into consideration any possible effect due to interaction with the solvent and care should be taken when applying it to very concentrated solutions. In the case of halides, Ikenmeyer[8] has found it to hold good over wide ranges of concentration.

9. CURIE BALANCE

A most successful magnetic balance was devised by P. Curie[9] in 1895, which he employed for his classical researches on magnetic properties of various substances at different temperatures.

It is a torsion balance in which the force exerted on any material when placed in a non-uniform field is measured in terms of the torque required to bring the specimen under examination back to the original position. In the original apparatus the non-uniform field was provided by means of two electromagnets with inclined axes. But in an improved portable apparatus convenient to work anywhere (1909) a permanent magnet of the shape shown in Fig. 15 was employed. The substance to be tested is placed in a glass tube suspended by the hook C from one end of an arm TT which is suspended by a silk or quartz fibre J. The other end of the arm TT carries a copper sector moving in the gap of a flat permanent magnet A which acts as an effective damping magnet due to eddy currents produced in the moving copper sector. Weights B and P are used to balance the system and keep the arm TT horizontal. A mirror helps in the accurate reading of the deflections. By means of an arm and two strings shown in Fig. 15 the permanent magnet can be turned concentrically downwards. In operating the apparatus the magnet is slowly turned so as to recede from the

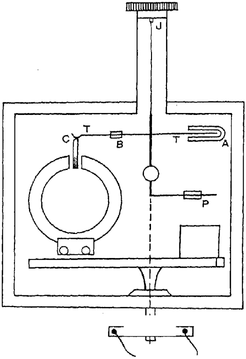

FIG. 15.—Curie-Chéneveau Balance with Permanent Magnet.

specimen. This is continued and observations are made when the deflection produced on the suspended system reaches a maximum. Readings are taken for deflections on both sides of zero. For calibrating purposes distilled water is used as a standard substance.

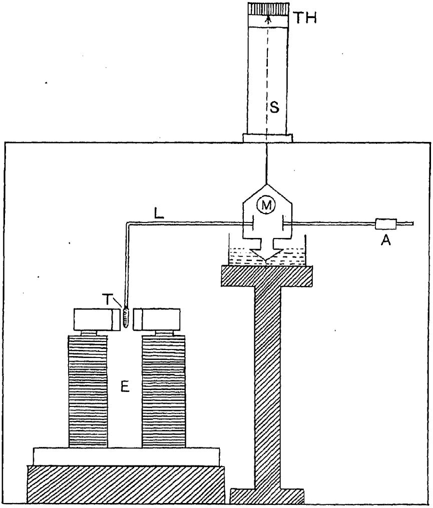

Fig. 16.—Curie-Wilson Balance.

TH = torsion head.
S = phosphor bronze suspension.
M = mirror.
E = electromagnet.
T = specimen tube.
L = aluminium arm.
A = sliding weight.

Observations are first made on the empty glass tube and then with the substance. The susceptibility is easily calculated from

$$\frac{\kappa}{\kappa_1} = \frac{m_1}{m} \cdot \frac{\theta \pm \theta''}{\theta_1 \pm \theta''}$$

where κ is the susceptibility of the substance under examination, m the mass of the substance, m_1 the mass of water, θ and θ_1 deflections for substance and water, respectively, and θ'' is the deflection for the empty tube. The sign + for θ'' is to be used if the tube has a susceptibility opposite to that of the body under examination. A correction for the susceptibility of the air has also to be made.

Two modifications of the Curie balance, which have been considerably employed by investigators, are due to Wilson[10] and Oxley.

10. CURIE-WILSON BALANCE

As shown in Fig. 16, the horizontal aluminium rod L is bent at right angles at one end and passed through an aluminium strip which carries the suspension wire of phosphor bronze (10 cm. length) at the upper portion and a damping vane working in a dashpot of oil at the lower end. The bent portion moves at a radius of about 11 cm. from the suspension and carries at the lower end arrangement for suspending a small glass bottle T. This is filled with the specimen up to a definite mark and suspended from the ring at the bent end of the aluminium rod.

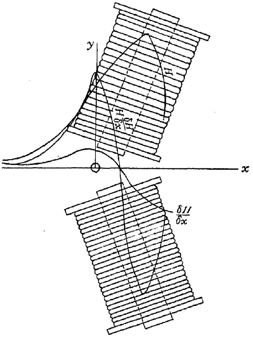

FIG. 17.—Field-gradients in Curie-Wilson Balance.

Counterbalancing of the specimen is brought about by the aluminium sliding weight A. The position of the torsion head and the mirror having been read, the field is produced in the magnet by passing a constant current from the storage batteries, as a result of which the specimen, being diamagnetic, is thrown out of the magnetic field. The pointer attached to the torsion head is now gradually moved to bring the specimen back to the original position and the torsion noted. Three torsion readings are required for each susceptibility determination: (i) torsion due to tube only; (ii) torsion with tube containing pure water; (iii) torsion with tube containing specimen. Of these (ii) is for calibrating the apparatus. The specific susceptibility is determined according to the following equation:

$$\chi = \frac{1}{M}\left\{ m_a . \chi_a + (\chi_w . m_w - \chi_a . m_{aw}) \frac{D - D_1}{D_2 - D_1} \right\}$$

where χ = susceptibility of air (210×10^{-7}),
χ_w = susceptibility of water ($-7{\cdot}25 \times 10^{-7}$),
M = mass of the specimen,
m_a = mass of air occupying the same volume as the specimen,
m_w = mass of water,
m_{aw} = mass of air occupying the same volume as water,
D = torsion due to tube + specimen,
D_1 = torsion due to tube alone,
D_2 = torsion due to tube + water.

11. OXLEY MAGNETIC BALANCE[11]

Oxley's balance differs from the Curie and Wilson balances in the method of recording readings. While in the other two balances the torsion head has to be carefully adjusted—a matter which occupies time—the Oxley balance uses a bifilar suspension DME carrying a mirror M. The specimen is not allowed to move appreciably from its zero position in the field, and consequently the force F (cf. equation 3) on the specimen is proportional to the deflections of the bifilar mirror.

In Fig. 18 the torsion arm, ABCD, is made of aluminium. The angle through which the arm is twisted, when the magnetic field is excited, is measured by the double suspension mirror. The dash-pot P contains a mixture of paraffin-oil and heavy mineral oil in which the four vanes V are free to move. The arm EF is capable of vertical and sideway movements. The rod GH provided with the cranks, C_1 and C_2, is used to rest the torsion arm to facilitate attaching the substance under investigation to the end A. To preserve balance of the torsion arm when different masses of substance are used, a rider R is provided which can be moved by the rod L into different positions along the torsion arm. A very fine phosphor-bronze wire, attached to the projection B, suspends the movable parts of the system.

The displacement of the substance under the field was about 1/200 mm. in Oxley's experiments. This would not appreciably alter the sensitiveness of the bifilar suspension, and, therefore, the use of torsion to bring the body back to its initial position was not necessary.

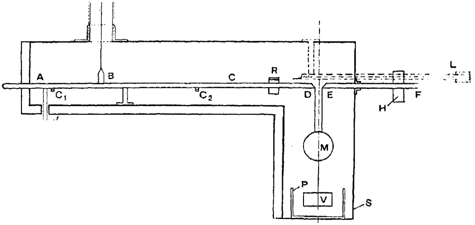

FIG. 18.—Oxley Balance.

Calculation of Susceptibility.—The force on the specimen in the field, from equation (9), is

$$F_x = (\chi_1 m_1 - \chi_2 m_2) H_y \frac{\partial H_y}{\partial x}$$

In Oxley's balance $F_x \propto D$ where D is the deflection on the scale, i.e. $F_x = pD$, p being a constant for small deflections.

Let d_1 be the deflection due to phial and contained air.
d_2 ,, ,, ,, and water,
d ,, ,, ,, and substance,
χ_a be the specific susceptibility of air,
χ_w ,, ,, ,, water,
χ ,, ,, ,, substance.

Then, from above,

$$p(d_2 - d_1) = (\chi_w m_w - \chi_a m_a) H_y \frac{\partial H_y}{\partial x} \quad . \quad . \quad (a)$$

$$p(d - d_1) = (\chi M - \chi_a M_a) H_y \frac{\partial H_y}{\partial x} \quad . \quad . \quad (b)$$

if the tube occupies the same position between the pole-pieces.

Here M is the mass of the substance taken, M_a that of the air which fills the same volume and m_a the mass of air which fills the volume m_w occupied by water. If the magnetic field is kept constant, the factor involving H on the right-hand side of (*a*) and (*b*) is constant, and we get by division:

$$\chi M = \chi_a M_a + (\chi_w m_w - \chi_a m_a) \frac{d - d_1}{d_2 - d_1}$$

The accepted values for the specific susceptibilities of water χ_w, and air χ_a, can be taken as $-7{\cdot}25 \times 10^{-7}$ and 210×10^{-7} (at 20° C.), respectively.

12. A MODIFIED CURIE BALANCE FOR GASES

A modified Curie balance for work on the susceptibilities of gases at low pressures has been described by Vaidyanathan[12] (Fig. 19).

It consists of a hollow glass bulb D, which is sealed and suspended from one end of a light aluminium bar AB, the latter being suspended by a torsion fibre. The bulb D is blown out of feebly diamagnetic glass selected by preliminary investigation on various specimens, and this diamagnetism is compensated for as nearly as possible by enclosing within it the requisite quantity of air. The bulb hangs in a suitable non-homogeneous field between the pole-pieces of an electromagnet. The bulb C, attached to the other end of the balance, counterpoises the weight of D, and in addition its volume is so adjusted that the hydrostatic buoyancy due to introducing gases into the balance-chamber is completely neutralised. The shape of the balance-chamber is suitably adjusted for the free movement of the balance within it. The chamber is connected to an elaborate arrangement for the introduction of gas and for altering of pressure. M is a mirror by which the deflections of the beam are read by the usual lamp-and-scale arrangement.

When the magnet is excited, the bulb is slightly attracted or repelled in vacuum owing to the imperfection in compensation and temperature fluctuations changing the susceptibility of the contained air. By rotating the torsion head, the balance is so adjusted that the beam lies along the axis of the chamber. Now, if a diamagnetic gas is introduced around the bulb, it apparently becomes more paramagnetic and is drawn towards the stronger part of the field, and on introducing a paramagnetic gas, it becomes diamagnetic to that medium and is repelled. The movement of the bulb D is adjusted to be in a perfectly horizontal plane and at right angles to the non-homogeneous field, causing a couple in the torsion fibre of the balance-beam. From the relative deflexions the volume susceptibility of one gas can be determined if the other is known.

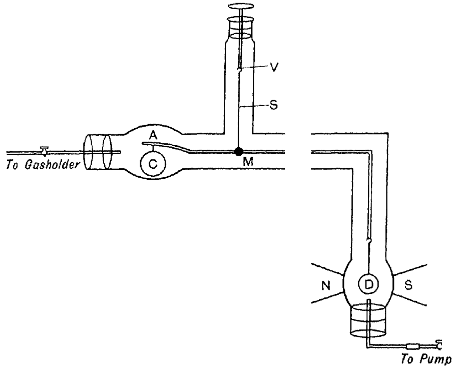

FIG. 19.—Vaidyanathan's Balance.

V = groove for suspension. M = mirror. S = phosphor-bronze strip.

13. THE INTERFERENCE BALANCE FOR MAGNETIC MEASUREMENTS

It is sometimes desirable to investigate susceptibilities of substances whose values are very close to each other. The balances described above are unable to give precise and reliable information on this point. An extremely sensitive balance which has the further advantage of stability and quickness of operation has been designed by Bhatnagar and R. N. Mathur[13]. The underlying principle of this balance is as follows:

If two converging beams of light are producing interference fringes and a moving glass plate be placed in the path of one, the shifting of the fringes will depend upon the movements of the plate and can be a measure of it. Moreover, very small movements of the plate will produce considerable shifting of the fringes. If, instead of measuring the movements of a spot of light on a scale, as in Oxley's balance, we measure the shift of the fringes produced by the movements of a glass plate, the apparatus will become considerably more sensitive. A Rayleigh interferometer provides interference fringes and possesses as well a convenient device for accurately measuring the shifting of the fringes. It was therefore adapted for this purpose. The apparatus is represented diagrammatically in Fig. 20.

In Fig. 20 ABC is a light aluminium or duralumin beam bent at right angles at B. The horizontal portion of the beam is carried in a light aluminium stirrup D, whose lower end has got cross-vanes E moving in a dash-pot F containing a medium-grade oil to damp the vibrations of the beam. The beam is suspended by a fine silver or phosphor-bronze strip. The other end of the suspension is attached to a brass rod G fixed to the torsion head H. I is a piece of optically plane parallel glass suspended by means of two silk threads J and K and carrying a damping vane partly submerged in an oil-bath. The thread J is attached to the end A of the beam, while the thread K is attached to the end of a horizontal rod L. The rod L passes through a hole at the end of the vertical rod M, and can be adjusted forwards or backwards in it. The brass rod M is attached by a screw to another torsion head N. The system LMN therefore provides a three-dimensional adjustment. Two riders O and P slide over the beam to keep it horizontal. The rider P is much lighter than O and is used for fine adjustment. Q is another optically plane parallel piece of glass of the same thickness as I, and is directly attached to the end of the rod R, which has similar movements to the system LMN. This is all enclosed inside a case, having a window in front. In order to move the riders O and P over the beam AB the arrangement of a chemical balance for moving the rider over its beam is fixed in a side of the box (not shown in the figure). The torsion arm AB can be supported when necessary on two cranks carried by the rod WX and capable of being manipulated from the outside of the box by the handle W. The arrangement for holding the phial consists of an aluminium piece bent at *b* and *d*, the pieces *b* and *d* having V-shaped holes, e_1 and e_2, through which the phial can be introduced. A thin rubber band passing over the stem of the phial secures it to the beam and holds it tight in the V-shaped holes. The top of the stem carries an etched mark, which serves to fix the position of the specimen phial with reference to another mark in the plate. By this means the phial is always replaced at the same position. Any change in the position of the phial, relative to the pole-pieces of the electromagnet, can now only be due to an alteration in the position of the beam AB, and this can be detected and removed by means of the interference fringes, as described later. The non-homogeneous magnetic field is obtained by inclining the pole-pieces of an electromagnet at an angle. The electromagnet is also placed inside the case containing everything else, and the whole case is fitted over a Hilger Interferometer in front of its small box containing the movable glass plate and the fixed compensating plate, in such a way that the two plates I and Q are in the path of the two parallel beams of light coming from the collimator.

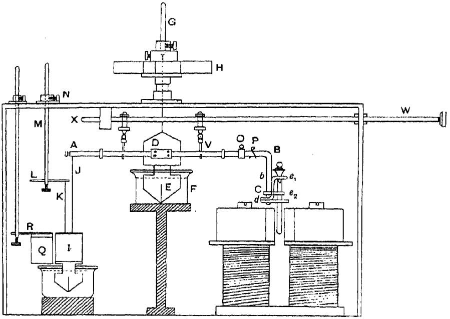

FIG. 20.—Magnetic Interference Balance. (Bhatnagar and R. N. Mathur.)

The parallel rays of light coming from the collimator pass through I and Q and then through the two plates in the box. The Hilger interferometer gives two sets of fringes lying side by side. One set is for reference only and the other shifts when the optical plate I moves. Using white light the central fringe is black when the two optical paths are identical, but when the plate is turned the optical path is changed and the black fringe shifts. The instrument carries an optical compensating arrangement with a measuring radial arm by which an equal path difference can be introduced in the other interfering beam and the black fringe brought back to the central position. Initially the black bands of the measuring and the reference systems are made to coincide. A known weight of the substance whose susceptibility is to be determined is then put in the phial and a constant current (about 1·5 amperes) taken from large-capacity batteries is passed in the electromagnet. On account of the movement of the phial in the field the glass plate I turns through an angle, and the upper system of fringes shifts to one side. The black band is again brought to coincidence by turning the micrometer screw of the compensating plate, and the number of divisions turned through are noted. Similar readings are taken for the empty phial and the phial containing a known weight of water.

The values for the specific susceptibilities are calculated by the following equation:

$$\chi \mathrm{M} = \chi_a \mathrm{M}_a + (\chi_w m_w - \chi_a m_a)\frac{r - r_1}{r_2 - r_1}$$

where the letters have the same significance as in Oxley's equation and r_1, r and r_2 are the readings on the interferometer for the empty tube, tube containing the specimen and tube with water, respectively. (A small instrumental correction has to be applied to the values of r.)

The sensitivity of this apparatus can be judged from the fact that a deflection of the tube of the order of 1/500 cm. corresponds to 600 divisions on the drum of the interferometer, and the accuracy of observations can easily be said to be within one in one thousand. With a very small weight of the substance, of the order of 0·01 gm., a change in diamagnetic susceptibility of the order of 0·2 per cent. or even less can, therefore, be easily detected.

14. MANOMETRIC BALANCES FOR MAGNETIC SUSCEPTIBILITY OF GASES

In their well-known investigation on gases, Wills and Hector[14] employed a manometric device on the Quincke principle. In the manometric balance the effect of the field on the gas is opposed to its effect on a standard solution of a paramagnetic salt like nickel chloride, and the exact point of balance is secured by changing the pressure of the gas or varying the temperature of the whole system. Bitter has used a modified form of Wills and Hector's method for his work on gases. His method dispenses with the use of the intermediate solution of a paramagnetic salt and compares the magnetic susceptibility of gases directly in terms of each other without resorting to very high pressures. In one arm of the manometer is admitted a mixture of gases from the reservoirs A_1 and A_2 (Fig. 21), while in the other, the unknown gas from the reservoir B. The gas liquid interface in both the arms is brought between the pole-pieces M. This is accomplished by means of the hinge and gear arrangement attached to the board N on which the arm GG is mounted. On applying an inhomogeneous field at M, a slight pressure difference between the regions in and out of the field results, and from the motion of the colloidal particles in the constriction E, observed through the microscope F attached to the wooden frame, it can be found as to which undergoes greater decrease in pressure, and hence which has the greater susceptibility.

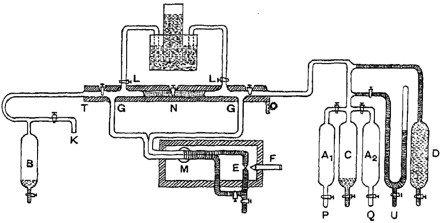

FIG. 21.—Bitter's Balance for gases.

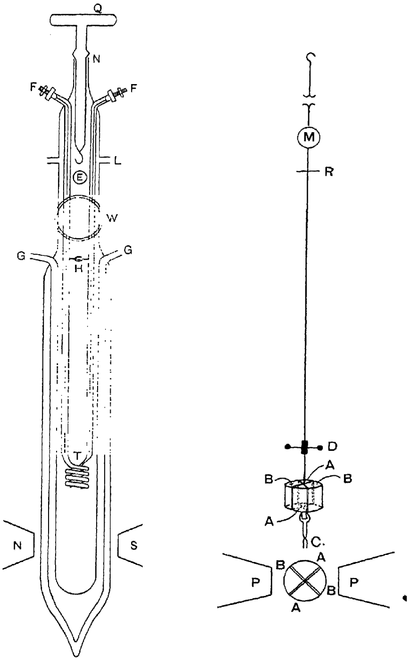

FIG. 22A and B.—Bitter's Balance for gases and vapours.

15. BITTER'S BALANCE FOR GASES AND VAPOURS

Bitter[15] has used another type of balance for his later work on gases and vapours in which a method originally due to

Glaser[16] has been modified. The method consists in measuring the orientative force exerted by a gas on a solid body suspended in a non-homogeneous field. The particular advantages of this method over those used by others lie in:

(i) That the test body is very symmetrical;

(ii) That it is made entirely of diamagnetic glass so that the magnetic forces acting on it are practically independent of temperature.

The test body (Fig. 22B) is made of Pyrex glass and consists of a cylindrical vessel to the top of which is fused a glass rod. The vessel is divided radially into four equal chambers. Two of these, A, are open to the surrounding gas, while the other two, B, can be evacuated through C and sealed off. D is a glass rod held by a tungsten spring and can be moved either vertically or rotated horizontally round the axis of the test body. With a vacuum in all the four quadrants, the rod D is moved up and down or twisted round until the test body hangs with the dividing walls parallel and perpendicular to the line joining the pole-pieces, no matter whether the field is off or on. If now, with field on, a gas be admitted to the chambers A, the test body will be deflected in such a way that A either moves towards or away from the pole-pieces according as the gas is paramagnetic or diamagnetic.

16. A BALLISTIC SUSCEPTIBILITY BALANCE

A susceptibility balance working on ballistic principle has been recently designed by Bhatnagar and K. N. Mathur[17]. In this method the force due to the field acts only during a short interval of time and thus imparts a momentum to the suspended system. The 'throw' of the suspended system is then a measure of the force acting. The suspended system consists of a beam of aluminium of the form shown in Fig. 23. *ab* is a central rod about 0·3 cm. thick and 9 cm. long. *c* and *d* are two cross-strips about 3·5 cm. long, 1 cm. wide and 0·15 cm. thick. At *g* and *h* are two sets of holes 0·35 cm. in diameter in each of the strips and very symmetrically placed from the centre. They serve to carry two similar glass tubes *e* and *f* made of carefully selected diamagnetic glass. The tubes are 5 cm. long and weigh about 0·2 gm. each. Two light pieces of mica, m_1 and m_2, serve to give the required damping. The suspension consists of a strip of phosphor bronze 5 cm. long. The specimen tubes are symmetrically placed in two non-uniform fields with gradients directed in opposite directions.

The pole-pieces have the special form shown in Fig. 23; the gap between them carries a third cylindrical pole-piece rigidly fixed in the centre. The three pole-pieces thus give two non-homogeneous fields of equal strengths, but oppositely directed.

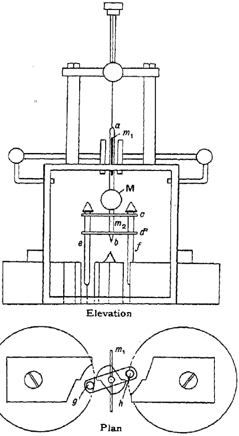

FIG. 23.—Ballistic Susceptibility Balance.

The two specimen tubes containing equal quantities of the substance under test are thus acted upon by a couple directed so as to pull the tubes within the strongest field if the specimen is paramagnetic and away from the field if the substance is diamagnetic.

The ballistic method dispenses with the torsion-head settings. Suppose the beam is initially at rest with the specimen tubes at some determined position within the pole-pieces. If now the electromagnet is excited for a short interval of time, an impulse will be imparted to the suspended system. The field current is switched off before the beam has moved through any appreciable angle and so the impulse would all be imparted at the rest position of the beam. Since the mechanical force on the specimen is

$$F_x = (\chi_1 M_1 - \chi_a M_a) H_y \frac{\partial H_y}{\partial x}$$

the impulse during a time T would be

$$(\chi_1 M_1 - \chi_a M_a) \int_0^T H \frac{\partial H}{\partial x} dt$$

If T be the period of free oscillation of the beam, θ the ballistic throw, then it can be shown that

$$(\chi_1 M_1 - \chi_a M_a) = k . T\theta$$

where k is an instrumental constant, provided that the time during which the field acts is kept constant and the zero-position of the specimen tubes remains the same with respect to the pole-pieces. The constant timing of the current in the electromagnet was obtained by a simple device described by K. N. Mathur and Lahiri,[17] making use of a commercial photographic 'self-timer' as the constant timing instrument.

As in the Oxley and Wilson methods three sets of observations are recorded: (i) throw with the empty specimen tube, (ii) throw with the tubes containing pure water, and (iii) throw with the tubes containing the substance. The period of oscillation T has to be found for each case.

The mass susceptibility is then calculated according to the formula:

$$\chi = \frac{1}{M}\left\{\chi_a M_a + (\chi_w M_w - \chi_a m_a) \frac{T\theta - T_1\theta_1}{T_2\theta_2 - T_1\theta_1}\right.$$

where χ, M, χ_w, M_w, χ_a, M_a, m_a have the same significance as in the Oxley balance (p. 45) and

θ = throw with tubes containing substance,

T = the corresponding oscillation period,

θ_1 = throw with empty tubes and T_1 oscillation period of empty tubes,

θ_2 = throw with tubes containing water and T_2 oscillation period.

It has not been possible to include here the description of several other magnetic balances which have been successfully employed in important magnetic investigations. Decker[18] employed a balance for liquids, working on non-homogeneous field principle, in which orientative force is exerted on a test body immersed in the liquid of which the susceptibility is to be determined. The balance is extremely convenient for making comparative measurements and deserves to be better known. Sucksmith[19] employed a magnifying arrangement of two mirrors fixed in a loop of phosphor bronze ribbon by which a movement of the specimen of 10^{-5} cm. could produce an observable effect in the measuring microscope. With ·5 gm. of a substance, susceptibility differences of the order of 10^{-6} could be easily measured. Rankine's[20] balance possesses the very novel feature of having a permanent magnet as its moving system.

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CHAPTER IV

PAN-MAGNETISM OF MATTER

REFERENCE has already been made to the early history of the subject of magnetism. Faraday was the first to establish the pan-magnetism of matter by showing that all substances were either attracted to or repelled away from the position of maximum magnetic field. The subject, however, did not assume a quantitative basis till much later.

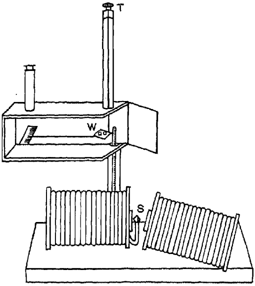

FIG. 24.—Curie's Balance.

S=specimen. W=weights for counterpoising. T=torsion head.

Curie's experimental researches on magnetic properties of substances in relation to temperature (1895), Honda's work on elements and Pascal's work on organic compounds constitute the pillars on which the modern theory of magnetism has been raised.

1. CURIE'S WORK

Curie[1] started his work in the belief that the effect of temperature on the dia-, para- and ferromagnetic substances would clear up the question whether the magnetism in these three physically distinct types, was fundamentally different or not. For susceptibility measurements Curie adopted the Faraday method but later on improved it by devising an instrument of greater accuracy and precision. The heating oven employed by Curie consisted of a porcelain tube round which was wound a double filament of platinum wire. A larger porcelain tube surrounded this tube and the space in between was filled with calcined magnesia or kaolin. Outside this was a water-jacket. A thermocouple suitably calibrated was employed for the purpose of noting temperatures, which could be controlled to a tenth of a degree, although it appears doubtful if the temperature of the specimen under examination, particularly at the higher temperatures, could be known with any accuracy, as the oven was unequally heated.

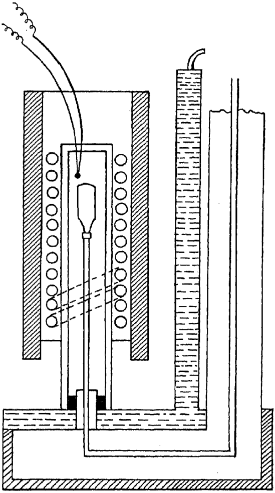
FIG. 25.—Curie's Heating Oven.

Curie's researches brought the following interesting points into prominence:

Diamagnetics.—Curie found that in diamagnetics the magnetic properties were generally independent of temperature and the field strengths. No change was noticed on melting in the susceptibilities of potassium nitrate and yellow phosphorus. Allotropic modifications in some cases were found to possess different susceptibilities. Yellow phosphorus, for example, was shown to have a value $0{\cdot}84 \times 10^{-6}$ and red phosphorus $0{\cdot}66 \times 10^{-6}$.

Paramagnetics.—To Curie goes the credit of discovering the most fundamental facts of paramagnetism. Working with oxygen over a range of temperature between 20° to 450°, Curie found that the following relation was held:

$$10^6\chi = \frac{33700}{T}$$

where T was the absolute temperature.

In the light of these results Curie re-examined the data of Wiedemann and Plessner[2] and found that the magnetic behaviour of the following paramagnetic substances, $FeCl_3$, $FeCl_2$, $NiSO_4$ and $Co(NO_3)_2$, was in line with the view that paramagnetic susceptibility is independent of the field strengths and varies, as a first approximation, inversely as the absolute temperature. The generalised formula

$$\chi = \frac{C}{T}$$

is known as Curie's Law.

Ferromagnetics.—Curie correlated the work previously done by Hopkinson[3] and others and carried out further investigations at higher temperatures. He made the important discovery that there is a critical temperature for every ferromagnetic substance at which it passes into the paramagnetic state. These substances are characterised by the fact that their susceptibilities vary with the field strength applied and on magnetisation the phenomena of hysteresis and remanence become prominent.

2. Honda and Owen's Work on Elements[4]

The pan-magnetism of matter raises the important issue as to whether the magnetic properties cannot be shown to be correlated with the ultimate structure of atoms and molecules. From a chemist's standpoint, the most interesting way of attempting to correlate physical properties with atomic structures is by examining these characteristics from the standpoint of the periodic table, or the arrangement of elements according to their atomic weights. As an example of the usefulness of this method may be cited the discovery of atomic numbers by Moseley from a comparison of the characteristic X-ray wavelengths of the elements and their position in the periodic table.

A rational electronic theory of magnetism had been proposed by Langevin (1905) long before the accurate values of susceptibilities of most elements were determined by Honda and Owen

(1910–1912). It is, however, more helpful to deal with the magnetic properties of elements in the first instance from the point of view of the periodic classification, and then to draw conclusions as to whether the atomic weight, the atomic number, the radii of constituent electronic orbits, singly or jointly, contribute to the magnetic properties of the elements. It is obvious that the difficulties of a close comparison are many, the most serious being the temperature at which the values of χ are to be compared, particularly in case of ferromagnetic and paramagnetic substances. It would be interesting to compare the atomic susceptibilities at corresponding temperatures, but the values of χ at these temperatures are not available. However, if elements are arranged in the form of a periodic table together with the values for specific and atomic susceptibilities certain regularities are at once apparent. In general, when the logarithms of magnetic susceptibilities against atomic numbers are plotted the elements belonging to the same group lie on a straight line. Before going into these details it would be worth while to study

TABLE I

A. *Diamagnetic Elements*

Atomic Number	Element	Specific Susceptibility $\chi \times 10^6$ 18° C	Gram-Atomic Susceptibility $\chi_A \times 10^6$	Temperature Range of Investigation ° C	Behaviour of Magnetic Susceptibility with Temperature
14	Silicon	−0·13	−3·65	−170 to 1000	Constant
15	Phosphorus	−0·90	−27·91	−170 to 120	Constant
16	Sulphur	−0·49	−15·70	−170 to 220	Constant
30	Zinc	−0·157	−10·26	−170 to 600	Constant, but falls suddenly on melting
33	Arsenic	−0·31	−23·23	−170 to 164	Constant
34	Selenium	−0·32	−25·34	−170 to 250	Constant
35	Bromine	−0·39	−31·16	−170 to 18	Constant
38	Strontium	−0·20	−17·52	−160 to 18	Constant
40	Zirconium	−0·45	−41·05	−170 to 400	Constant
50	Tin (Grey variety)	−0·35	−41·55	18 to 400	Constant, decreases suddenly on melting
79	Gold	−0·15	−29·58	−170 to 1230	Constant, but increases on melting
80	Hg (liquid)	−0·19	−38·12	−38 to 310	Constant
	(solid)	−0·15	−30·09	−130 to −80	Constant
82	Lead	−0·12	−24·86	−170 to 600	Constant, but decreases suddenly on melting

TABLE I (*continued*)

B. *Abnormal Diamagnetics*

Atomic Number	Element	Specific Susceptibility $\chi \times 10^6$ 18° C	Gram-Atomic Susceptibility $\chi_A \times 10^6$	Temperature Range of Investigation °C	Behaviour of Magnetic Susceptibility with Temperature
4	Beryllium	$-1·0$	$-9·02$	-170 to 300	Increases with temperature
5	Boron	$-0·69$	$-7·47$	-170 to 1100	,,
6	Carbon (diamond)	$-0·49$	$-5·88$	-170 to 1200	,,
	(Ceylon graphite)	$-6·0$ $(-170°$ C)	$-72·0$	-170 to 1150	Large decrease with temperature
29	Copper	$-0·086$	$-5·40$	-170 to 1050	Decreases slightly with temperature
31	Gallium	$-0·24$	$-16·73$	-170 to 100	Decreases slightly with temperature and suddenly on melting
32	Germanium	$-0·12$	$-8·71$	-170 to 100	Decreases with temperature, but sudden increase on melting
47	Silver	$-0·20$	$-21·56$	-170 to 1125	Increases with temperature
48	Cadmium	$-0·18$	$-20·234$	-170 to 700	Constant to 300° but decreases at high temperature
49	Indium	$-0·11$	$-12·63$	-170 to 150	Decreases with temperature
51	Antimony	$-0·87$	$-105·93$	-175 to 800	Constant to 50° but decreases at high temperature
52	Tellurium	$-0·31$	$-39·52$	-160 to 525	Decreases with temperature
53	Iodine	$-0·36$	$-45·69$	-160 to 160	Increases in the solid state, but decreases in the liquid state
81	Thallium	$-0·24$	$-49·05$	-18 to 440	Decreases with temperature
83	Bismuth	$-1·35$	$-282·15$	-259 to 600	Decreases with temperature and suddenly on melting

the behaviour of elements as far as their susceptibility variation with temperature is concerned. In Tables I and II are gathered together the values of specific and gram atomic susceptibilities of diamagnetic, paramagnetic and ferromagnetic substances. The tables have been further subdivided in two portions. Part A of Table I gives elements whose susceptibilities are not

TABLE II

Atomic Number	Element	Specific Susceptibility $\chi \times 10^6$ 18° C	Atomic Susceptibility $\chi_A \times 10^6$	Temperature Range of Investigation	Behaviour of Magnetic Susceptibility with temperature
	A. *Normal Paramagnetics*				
8	Oxygen (solid), S_2 state	118 * (-240° C.)	..	-240° to -219° C.	Decreases with temperature
8	Oxygen (liquid)	310 * (-219° C.)	..	-219° to -196° C.	,,
	Oxygen (gas)	106·2	1700	..	,,
22	Titanium	1·25	59·87	- 170° to 20° C.	,,
39	Yttrium	5·3	471·27	- 160° to 400° C.	,,
46	Palladium	5·4	576·1	-258° to 1230° C.	,,
58	Cerium	15·0	2101·0	-170° to 200° C.	,,
59	Praseodymium	25·0	3523·0	-170° to 970° C.	,,
60	Neodymium	36·0	5194·0	..	,,
68	Erbium	22·0 *	3688·0	..	,,
73	Tantalum	0·93	157·8	-170° to 820° C.	,,
78	Platinum	1·10	214·5	-170° to 1220° C.	,,
92	Uranium	2·6	619·1	..	,,
	B. *Abnormal Paramagnetics*				
3	Lithium	0·50	3·47	-170° to 16° C.	Constant
8	Oxygen (solid), S_1 state	54 * (-259° C.)	..	-259° to -240° C.	Increases with temperature
11	Sodium	0·51	11·728	-170° to 97° C.	Constant
12	Magnesium	0·55	13·36	18° to 700° C.	Constant
13	Aluminium	0·63	17·00	-170° to 1000° C.	Constant, slight decrease over 500° C.
19	Potassium	0·52	20·38	-170° to 190° C.	Constant
20	Calcium	1·10	44·08	-170° to 18° C.	Constant
23	Vanadium	1·4	71·33	-170° to 1100° C.	Increases with temperature
24	Chromium	3·7	192·43	-170° to 1100° C.	,,
25	Manganese	9·9 *	543·80	18° to 100° C.	Constant
37	Rubidium	0·21 *	17·94	-170° to 38° C.	Constant
41	Columbium	1·5	139·95	-170° to 450° C.	Constant
42	Molybdenum	0·04	3·84	18° to 1250° C.	Constant
44	Ruthenium	0·50	50·85	-170° to 1100° C.	Increases with temperature
45	Rhodium	1·11	114·23	-170° to 1140° C.	,,
50	Tin	0·025	296·0	18° to 400° C.	Constant
55	Caesium	0·22 *	29·21	-170° to 18° C.	Constant
56	Barium	0·9	123·62	-170° to 18° C.	Constant
57	Lanthanum	1·04	144·47	-170° to 18° C.	Constant
74	Tungsten	0·28	51·52	-170° to 1100° C.	Constant
76	Osmium	0·05	9·54	-170° to 1100° C.	Constant
77	Iridium	0·15	28·96	-170° to 1150° C.	Increases with temperature
90	Thorium	0·13	30·16	-170° to 390° C.	,,

* Values taken from more recent work.

influenced by temperature, and they may be called normal diamagnetics. Part B includes elements whose diamagnetic susceptibilities show a variation with temperature. In Part A of Table II are given the normal paramagnetic elements whose susceptibilities decrease with increasing temperature. Part B of this table deals with paramagnetic substances whose susceptibilities either remain constant or increase with temperature. Iron, nickel and cobalt are classed as ferromagnetics and their susceptibility varies with the field strength applied. They form an important class by themselves and are specially discussed in a later chapter in this book.

3. MAGNETIC PROPERTIES IN RELATION TO PERIODIC CLASSIFICATION

An examination of the data on magnetic susceptibilities as given in Tables I and II and the Periodic Table Chart indicates that the value of χ_A does not increase regularly with atomic numbers but varies periodically with it. A more careful analysis reveals among others the following significant facts:

(i) The gram-atomic susceptibility of the elements in each of the groups generally increases with the atomic number. There are some exceptions to it which are discussed later.

(ii) The inert gases are all diamagnetic. The gram-atomic susceptibilities of helium, neon and argon are in the order of their atomic numbers. Experimental values for Kr, Xe and Nt are not available.

(iii) For groups I to VII the elements constituting the sub-group *a* are generally paramagnetic, while those belonging to the sub-group *b* are mostly diamagnetic. This will be clear from the following:

Group I

Sub-group *a*. Li (3), Na (11), K (19), Rb (37) and Cs (55) * are all paramagnetic.

The atomic susceptibilities increase in the above order, though rubidium appears to be slightly erratic. The susceptibilities of these metals do not vary with temperature except for Li, for which reliable data are not available.

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* Cs has been described as diamagnetic in the International Critical Tables. Recent measurements by Lane[5] give it a definitely paramagnetic value $\chi = +0{\cdot}22 \times 10^{-6}$.

Sub-group *b*. Cu (29), Ag (47) and Au (79) are all diamagnetic and conform to the general rule.

Group II

Sub-group *a*. Of the sub-group *a* consisting of Ca (20), Sr (38), Ba (56) and Ra (88), Ca and Ba are both paramagnetic; Sr is exceptional as it is diamagnetic. The value for Ra is not known. All these elements, however, are similar in as much as their susceptibilities show no variation with temperature.

Sub-group *b*. Be (4), Zn (30), Cd (48), Hg (80) are all diamagnetic. Mg (12) is weakly paramagnetic but it behaves like a normal diamagnetic in the respect that its susceptibility does not show any variation with temperature.

Group III

Sub-group *a*. Y (39) together with the rare earths La (57), Ce (58), Pr (59), Nd (60), Er (68) are known to be paramagnetic. Of the remaining elements Sc (21), Ac (89) and the rest of the rare earths (atomic numbers 61 to 67 and 69 to 71) have not so far been investigated as elements. They may, however, be expected to behave as paramagnetics in view of the strongly paramagnetic salts which they give.

Sub-group *b*. Of the elements B (5), Al (13), Ga (31), In (49) and Tl (81) constituting this sub-group, all except Al are diamagnetic. Aluminium, though paramagnetic, behaves like a typical diamagnetic in showing no susceptibility variation with temperature.

Group IV

Sub-group *a*. This is an exceptional group. Though Ti (22) and Th (90) are both paramagnetic, their susceptibilities are in the inverse order of their atomic numbers. Zr (40) is an exception as it is diamagnetic. The value for elemental Hf is not known.

Sub-group *b*. C (6), Si (14), Ge (32), Sn (50) and Pb (82) are all diamagnetic, but their susceptibilities do not seem to obey any regular order of variation with atomic number. Thus carbon ($\chi_A = -5{\cdot}88 \times 10^{-6}$) is more diamagnetic than Si ($\chi_A = -3{\cdot}65 \times 10^{-6}$). The next elements Ge ($-8{\cdot}71 \times 10^{-6}$), Sn ($-41{\cdot}5 \times 10^{-6}$) show regular increase in susceptibility with Si, but Pb ($\chi_A = -24{\cdot}86 \times 10^{-6}$) is again an exception.

Group V

Sub-group *a*. V (23), Cb (41), Ta (73) are all paramagnetic with the gram-atomic susceptibility regularly increasing with the atomic number. Value for Pa (91) is not known.

Sub-group *b*. N (7), P (15), As (33), Sb (51) and Bi (83) are all diamagnetic, following the rule of variation, with the exception that As has slightly lower value than P, and Sb and Bi have numerically high atomic susceptibilities.

Group VI

Sub-group *a*. Cr (24), Mo (42), W (74), U (92) are all paramagnetic and follow the general rule, with the exception of Cr, which has a much higher magnetic susceptibility than either Mo or W.

Sub-group *b*. Only oxygen (8) at the head of the sub-group is strongly paramagnetic, while the rest of the elements, viz. S (16), Se (34), Te (52), are diamagnetic. The susceptibility for Po (84) is not known. The case of oxygen is of particular interest and has been fully discussed elsewhere.

Group VII

Sub-group *a*. Only manganese (Mn 25) has been investigated so far and is found to be paramagnetic. Values for Ma (43) and Re (75) are not available.

Sub-group *b*. Cl (17), Br (35), I (53) are all diamagnetic and their atomic susceptibilities increase regularly in the order of their atomic numbers. F (9) has not yet been investigated.

(iv) Elements of the transition series occupying group VIII in the periodic classification are characterised by very peculiar magnetic properties. The transitional elements of the first long period, viz. Fe (26), Co (27) and Ni (28), are ferromagnetic; the ferromagnetism lapses into paramagnetism above a certain temperature known as the Curie point. In these elements the susceptibility instead of increasing with the atomic number shows a decrease. For example, Fe (26) is ferromagnetic while Ru (44) has $\chi = 50{\cdot}85$ and Os (76) has a still smaller susceptibility $\chi = 9{\cdot}54$. Similarly Co (27) is ferromagnetic. Rb (45) has a greater gram-atomic susceptibility than Ir (77). Ni (28) again is ferromagnetic while Pd (46) has a higher susceptibility value than Pt (78).

(v) If the elements are considered as periods, the following regularities become evident:

PERIOD IV (THE FIRST LONG PERIOD)

Even Series.—The elements K (19) to Mn (25) are all paramagnetic with susceptibilities which increase with atomic number. The value for Sc (21) is not known, but by analogy we should expect it to be paramagnetic also. The ferromagnetic elements Fe (26), Co (27), Ni (28) belong to this period.

Odd Series.—Cu (29) to Br (35) are all diamagnetic. The order of diamagnetic values increases from $\chi_A = -5{\cdot}40 \times 10^{-6}$ to $\chi_A = -31{\cdot}16 \times 10^{-6}$, Ge (32) being an exception.

PERIOD V (THE SECOND LONG PERIOD)

Even Series.—The elements Rb (37) to Pd (46) are paramagnetic excepting Sr (38) and Zr (40) which are diamagnetic. Ma (43) is not so far investigated.

Odd Series.—All the elements from Ag (47) to I (53) are diamagnetic.

PERIOD VI

Even Series.—The elements Cs (55) to Pt (78) are all paramagnetic. Hf (72) and Re (75) have not been investigated so far. This series includes also the rare earths La (57) to Lu (71), for many of which the elemental susceptibilities are not known.

Odd Series.—The elements Au (79) to Bi (83) are all diamagnetic. Po (84) has not been investigated, but on analogy it should be diamagnetic.

PERIOD VII

Th (90) and U (92) are paramagnetic. The values for Ra (88), Ac (89) and Pa (91) are not known, but they may be expected to be paramagnetic.

4. MAGNETISM AND ALLOTROPY

While studying the physical properties of elements one is sometimes struck with the remarkable property of some of the elements in being able to exist in more forms than one. These forms, known as allotropes, differ from one another considerably in colour, density, solubility and even in chemical reactivity. The discussion on magnetic susceptibility in relation to periodic table would be incomplete without a brief reference to this aspect of the subject. Further, on account of a revival of interest in Faraday's magnecrystallic effect, this subject has acquired special importance during recent years. Careful work accomplished within the last few years has established that allotropic forms differ, sometimes considerably, from one another in magnetic properties. In the following table are given the specific susceptibility values of some of the elements existing in allotropic forms:

TABLE III

Element	Susceptibility. $\chi \times 10^6$	Author
Sulphur—		
Rhombic . .	−0·487	Bhatnagar and Mathur[6]
Monoclinic .	−0·462	,,
Plastic . .	−0·4 (approx.)	,,
Colloidal . .	−0·510	Owen[7]
Phosphorus—		
Yellow . .	−0·84 to 0·90	Curie[8]
Red . .	−0·66	,,
Tin—		
Grey . .	−0·35	Honda[9]
White . .	+0·025	Honda[10]
Carbon—		
Graphite . .	−3·5	Owen[7]
Diamond .	−0·49	Honda[10] and Owen[7]
Lamp black .	−0·36 to −0·53	Paramasivan[11]
Gas Carbon .	−2·0	Honda[9]
Oxygen—		
O_2 . . .	+104·7	Curie[8]
O_3 . . .	Paramagnetic (highly)	Becquerel[12] (1881)
	Feebly paramagnetic or diamagnetic	Wulf[13] (1928)
	Diamagnetic	Vaidyanathan[14] (1928)
O_3 liquid . .	Paramagnetic	P. Laine[15] (1933)

The value of χ for ozone has been a disputed question. Vaidyanathan, both from investigations of ozonides as well as ozonised oxygen, came to the conclusion that this gas was diamagnetic. P. Laine[15] has, however, recently revised this and finds that magnetic measurements on ozonised oxygen give discordant results, but the liquid ozone shows a distinct paramagnetism independent of temperature.

5. PASCAL'S CLASSICAL WORK ON COMPOUNDS[16]

If the comparison of physical properties according to the periodic classification of elements has yielded valuable information regarding the electronic structure of atoms, no less important have been the achievements of the chemist in connection with molecule-building from an examination of physical properties in closely related groups.

As regards magnetic properties and chemical constitution the master mind has been that of Pascal, who, in a series of extensive magnetochemical investigations extending from 1908 to 1913, carefully studied the influence of chemical combination on the magnetic properties of compounds. As a matter of fact the importance of Pascal's work in magnetochemistry is comparable to the classical researches of Curie on the subject of paramagnetism.

Pascal's extensive researches can roughly be classified under three heads:

(i) Complex compounds.
(ii) Metalloids and gases.
(iii) Organic compounds.

In this chapter it is proposed to give a brief survey of Pascal's investigations, reserving the discussion of more recent work on the subject to another chapter as the subject has been considerably extended in recent years owing to better understanding of atomic behaviour and molecular architecture. In view of the large number of compounds studied by Pascal, it is impossible to make more than a passing reference to many of them. Reference must be made to the original memoirs for fuller details.

(i) *Complex Compounds.*—Wiedemann[17], following the earlier work of Plücker[18], published a considerable amount of work from 1865 to 1878 on the salts of ferromagnetic metals. He seems to have been the first to notice that the magnetic properties of iron and cobalt disappeared in the ferro-, ferri- and the cobalt cyanides. Wiedemann's suggestion that the magnetic properties of a metal in combination were due to the mode of grouping of the atoms was verified by the more precise work of Townsend[19], Liebknecht[20] and Wills[21] and of St. Meyer[22]. No general law connecting magnetic with chemical properties was, however, known or suggested, and it was left to Pascal to generalise from his vast data and evolve conclusions connecting the magnetic and chemical properties. Recent work on the complex compounds has made us revise many of the conclusions arrived at by Pascal, but this has been the result of our changed conceptions of the whole subject of magnetism in view of the recent developments of the theory rather than of any inherent defect in Pascal's work.

As Pascal worked mostly on solutions and liquids, he employed a modified Quincke's U-tube method and measurements were taken for several different concentrations of solutions. The susceptibilities determined by him referred to χ for water $= -0{\cdot}75 \times 10^{-6}$. The absolute values, therefore, require to be corrected as the present accepted value for the susceptibility of water is $-0{\cdot}72 \times 10^{-6}$.

The first group of substances investigated by Pascal included the alkali ferri- and ferrocyanides, meta and pyrophosphates, ammoniacal citrates, alkali ferroxalates, etc.

It is known that the pyrophosphates and meta-phosphates of metals of the Fe group dissolve in the solution of corresponding salts of alkali metals, giving complex salts, the composition of which resembles that of complex cyanides where the group $(CN)'$ is replaced by $(P_2O_7)''''$ or $(PO_3)'$. The most stable compounds are ferri-pyrophosphates and the ferro-pyrophosphates which were studied in much detail. It was easy to prepare from them the corresponding Na, Ag, Cu and other similar compounds. A number of ammoniacal complexes akin to the cobalt-ammines could also be easily prepared.

In each of these substances a close parallelism between the magnetic and chemical characteristics of the iron was fully established. Thus a solution of ammoniacal ferric-pyrophosphate containing 2·1 gm. of Fe per litre has a magnetic susceptibility $\chi = -0{\cdot}453 \times 10^{-6}$. If hydrochloric acid is added to it to bring it back to the initial titration value the susceptibility becomes $\chi = -0{\cdot}235 \times 10^{-6}$.

In this experiment the return towards the paramagnetism of the ferric-pyrophosphate solution cannot be attributed to the ammonium chloride produced as that is in itself diamagnetic. Moreover, the return of the paramagnetism is accompanied by the reappearance in the solution of the analytical characteristics of the normal ferric salts. From his study of the ferrous salts and their ease of oxidisability, Pascal concluded that the complex ferrous salts are more oxidisable in solution in proportion as the paramagnetism of the iron which they contain becomes more apparent analytically.

The cobalt salts studied included the chloride, the ammoniacal chloride, the double phosphate and the luteo-chloride. Of these the luteo-cobaltic chloride was diamagnetic. Among the other substances studied were the sulphate, pyrophosphate and permanganate of manganese, the violet and green chrome alums and chromic acid; copper sulphate, glycerinated and ammoniacal copper sulphate and Fehling's solution, the chloride, cyanide, chlor-mercurate and iodomercurate of mercury, etc. It was noticed that in the case of the permanganate the formation of the complex ion $(MnO_4)'$ is accompanied by a remarkable diminution of the susceptibility of the highly paramagnetic Mn ion. Chromic acid was found to be feebly diamagnetic, in close agreement with the disappearance of the characteristic reactions. Copper offered an example of a new kind. It is diamagnetic in the metallic state but strongly paramagnetic in its compounds. This acquired paramagnetism becomes much attenuated in the complex ions. Mercury is a diamagnetic metal. Its chloride, cyanide and the double chloride with potassium were all found to be diamagnetic, but potassium iodomercurate on the other hand, which is known to contain mercury in the complex state, loses its diamagnetism to such an extent as to become paramagnetic.

Apart from the cases in which the complexity is chiefly due to the passage of the metal from the cation to the anion, Pascal made a study of the metals like vanadium and uranium which give complex oxygenated radicals playing the part of 'cation' and can also give oxygenated anions. The uranium salts studied were uranous sulphate, $U(SO_4)_2$, and acid uranyl sulphate, UO_3SO_4. The former was found to be paramagnetic and the latter diamagnetic. It was interesting to note that a strongly paramagnetic element like oxygen, far from increasing the paramagnetic properties of the metal, actually makes it appear diamagnetic. At the same time the chemical reactions of the ion are also completely masked.

The vanadium salts studied were vanadium di-chloride, VCl_2, tetrachloride, VCl_4, acid sulphate of divanadyl, $V_2O_2(SO_4)_2$, and acidified solutions of vanadic anhydride. Of these VCl_2, VCl_4 and $V_2O_2(SO_4)_2$ were paramagnetic, while $Na(VO_3)$ and the acid solutions of V_2O_5 were diamagnetic. The conclusion was therefore inevitable that the strongly paramagnetic oxygen when forming a complex ion—whether anion or cation—always completely masks the magnetic as well as the chemical properties of the metal concerned.

As the normal chemical properties of metals are masked in the colloids prepared from them, it follows that their magnetic properties might likewise be completely masked. This was experimentally verified by Pascal in the case of a few colloids. The substances studied were ferric hydroxide sol containing 4·93 gm. of Fe, copper ferrocyanide sol containing 2·36 gm. of Cu and ferric acetate sol containing 2·85 gm. of Fe per litre. In each case a large change in the magnetic properties of the metal was clearly observed.

(ii) *Metalloids and Gases.*—The halogens chlorine, bromine, iodine and the two families of metalloids, sulphur, selenium, tellurium and phosphorus, arsenic, antimony and bismuth were studied by Pascal, as also a number of easily liquefiable gases, e.g. sulphur dioxide, ammonia, cyanogen, nitrous oxide, nitrogen peroxide, methylamine and methyl chloride.

The measurements were made mainly on liquids or liquefied gases by a fairly simple form of U-tube method. One of the branches of the U-tube was widened and had an internal diameter of 10 mm. and the other was only 4 to 5 mm. wide. The tube could be immersed completely in a mercury bath cooled to about -75° when it was half filled with the liquefied gas and removed from the freezing mixture. The two extremities of the U-tube were then immediately sealed. For measurements the narrower arm was placed vertically between the poles of an electromagnet, with the wider arm outside the field. The depression of the meniscus was noted when the field was excited and compared with that given by the same tube filled with distilled water.

The specific susceptibility of the liquids was calculated by the formula

$$\chi = \frac{\chi_0}{\rho} - 7{\cdot}75\lambda \, . \, 10^{-7}$$

where χ_0 is the correction for the susceptibility of the medium. This correction was carefully worked out in each case from a knowledge of the physical factors such as temperature and pressure inside the tube, the atmospheric temperature and pressure and the vapour tensions of the liquefied gas at the temperature of the experiment, etc.

From a study of the measurements made by Pascal, as also from the previous values given by Curie, it was apparent that no simple relation seemed to exist between the diamagnetic susceptibility of an element and its atomic weight. When, however, the elements were classified in families or groups according to the Periodic Table, Pascal found that the atomic susceptibility increased regularly with the atomic weight, as is shown by the following figures:

		$-\chi \times 10^6$	$-\chi_A \times 10^6$
First family . . .	Cl	0·590	20·95
	Br	0·899	31·92
	I	0·366	46·5
Second family . .	S	0·487	15·6
	Se	0·303	24·0
	Te	0·311	38·9
Third family . .	P	0·887	27·4
	Sb	0·646	77·5
	Bi	0·910	189·6

The diamagnetic susceptibility in each of the above families is related to the atomic weights by an expression of the form

$$\chi_A = -10^{-7} . e^{\alpha+\beta A}$$

where A is the atomic weight and α and β are constants for each family. For Cl, Br, I $\alpha = 2·195$, $\beta = 0·00380$; for S, Se, Te $\alpha = 2·058$, $\beta = 0·00418$; for P, Sb, Bi $\alpha = 2·2806$, $\beta = 0·00505$.

It may be noted here that the first members of each family of elements or group of compounds often do not obey any law. They are in general less diamagnetic than required by the formula. Oxygen, for example, which is the first member of the second group is paramagnetic.

A number of easily liquefied gases were used by Pascal and particular care was taken to free them from ferromagnetic impurities and dissolved oxygen. The susceptibilities were determined in the liquid state and the values for volume susceptibility in the gaseous state were deduced from them. The values obtained (reduced to 0° C. and 760 mm.) are shown below, as also the gram-molecular susceptibilities:

	$-\kappa \times 10^{10}$	$-\chi_M \times 1$
SO_2	8·5	19·0
NH_3	8·5	19·0
C_2N_2	10·1	22·5
N_2O_3	10·3	23·2

	$-\kappa \times 10^{10}$	$-\chi_M \times 10^6$
N_2O_4	11·3	25·3
CH_3NH_2	12·5	28·1
CH_3Cl	15·1	33·3
Cl_2	18·7	41·9

It was noticed that for all except the last two gases the molecular susceptibility increases regularly with the number, n, of the atoms contained in the molecules. Pascal expressed this by the formula:

$$\chi_M = -23{\cdot}3(5+n) \times 10^{-7}$$

or

$$\kappa = -1{\cdot}04(5+n) \times 10^{-10}$$

This relation does not seem to have any particular importance or significance.

(iii) *Organic Compounds*.—The most significant contribution which Pascal made to the theory of diamagnetism is the discovery of the principle of the additivity of the diamagnetic properties of organic compounds. He showed that the molecular susceptibility χ_M of a compound having the formula $A^\alpha B^\beta C^\gamma$ can be given by the equation

$$\chi_M = \Sigma\alpha\chi_A + \lambda$$

where α, β, . . . are the number of atoms of susceptibility χ_A, χ_B, . . . and λ is a constitutive correction constant, depending upon the nature of the chemical linkages.

A few examples will serve to make Pascal's procedure clear. Taking the mono-halogen derivatives of benzene it was found that the differences between the molecular susceptibilities χ_M of chlorobenzene and bromobenzene and between bromobenzene and iodobenzene were the same as the corresponding differences between the atomic susceptibilities of the halogens themselves. The atomic susceptibility of hydrogen was then determined by replacing an atom of the halogen by hydrogen and finding the change in the molecular susceptibility. The following groups of compounds will illustrate this:

SUBSTITUTION DIFFERENCES FOR Cl (PASCAL)

	$-\chi_M \times 10^6$	Difference
Ethyl acetate, $CH_3.CO_2C_2H_5$	57·5	17·8
Ethyl chloracetate, $CH_2Cl.CO_2C_2H_5$	75·3	
Acetone, CH_3COCH_3	35·1	17·9
Chloracetone, $CH_2Cl.COCH_3$	53·0	
Benzene, C_6H_6	57·4	3 × 17·83
Trichlorbenzene, $C_6H_3Cl_3$	110·9	

The mean 17·85 thus represents the diamagnetic difference due to the substitution of Cl for H. Taking for atomic chlorine the value $\chi_A = 20{\cdot}95 \times 10^{-6}$, Pascal obtained for hydrogen the value

$$\chi_H = -10^{-6} \times (20{\cdot}95 - 17{\cdot}85) = -3{\cdot}1 \times 10^{-6}$$

Similar values for the susceptibility of H are obtained by comparing the derivatives of bromine and iodine.

The mean value for atomic diamagnetic susceptibility for H given by Pascal is

$$\chi_H = -3{\cdot}05 \times 10^{-6}\,*$$

The value for the CH_2 group was determined from the differences in the susceptibilities of the hydrocarbon series.

	$-\chi_M \times 10^6$	Difference
Aliphatic Series—		
Hexane, C_6H_{14}	79·6	2 × 12·05
Octane, C_8H_{18}	103·7	2 × 13·0
Decane, $C_{10}H_{22}$	129·7	
Ethylene Series—		
Pentene, $(CH_3)_2C{=}CHCH_3$	56·4	3 × 12·26
Octene, C_8H_{16}	93·2	
Aromatic Hydrocarbons—		
Benzene, C_6H_6	57·4	12·5
Toluene, $C_6H_5.CH_3$	69·9	12·2
Meta-xylene, $C_6H_4(CH_3)_2$	82·1	2 × 12·65
Para-cymene, $C_6H_4(CH_3)(C_3H_7)$	107·4	

These give the value of the CH_2 group $\chi_{CH_2} = -12{\cdot}32 \times 10^{-6}$.

Pascal obtains similar values for the CH_2 group from several different types of compounds, such as the series of primary alcohols, aldehydes, ketones, acids, aliphatic and aromatic amines; and also from the ethers, esters and even the sulphides of the type $(CH_3)_2S$, $(C_2H_5)_2S$, etc. These give the mean value $\chi_{CH_2} = -12{\cdot}35 \times 10^{-6}$. The value for carbon could also be similarly calculated on the additivity principle. We have, for example,

$$\chi_C = \chi_{CH_2} - \chi_{H_2} = \chi_{CH_2} - 2\chi_H$$

from which $\chi_C = -(12{\cdot}35 - 6{\cdot}1) \times 10^{-6} = -6{\cdot}25 \times 10^{-6}$

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* The value $-3{\cdot}05 \times 10^{-6}$ should be $-2{\cdot}93 \times 10^{-6}$ when corrected for the standard value for water $(-0{\cdot}72 \times 10^{-6})$ instead of Pascal's $-0{\cdot}75 \times 10^{-6}$. Other values of Pascal require similar correction.

This indirectly determined value is in remarkably good agreement with direct measurements on the carbon prepared from pure sugar.

Constitutive Correction Constant.

The determination of the constitutive correction constant λ in the additivity formula

$$\chi_M = \Sigma \alpha \chi_A + \lambda$$

requires careful investigation of a large number of compounds of similar type. Apart from the simplest type of compounds for which the correction constant is easily determined, there are numerous complicated organic structures where it becomes necessary to take into account all the various bonds and groups and their structural configurations relative to each other. In general, Pascal was able to affix certain definite values of the correction constant for many of the valency linkages and their mutual interactions and to show that they retain their identity in a large variety of compounds. It is necessary for the application of the additivity principles that the structure of the compounds should be correctly known. There had been considerable doubt about the constitution of many organic compounds, and in such cases the magnetic method was found to afford valuable evidence in support of one structure or the other. Pascal, however, points out many instances where the additivity values are not in agreement with experiment. This is true particularly of compounds containing nitrogen and the halogens. In such cases it has been found that the mutual interaction is so strong and variable that it not only affects the additivity principles of the magnetic susceptibilities but also other well-known properties such as optical refractivities, magnetic rotatory power, etc.

It has to be pointed out that the value of λ for a complicated structure is obtained as $\Sigma\lambda$ from the summation of the various corrective constants for the individual groups and linkages.

For a systematic study of the constitutive correction constants the organic compounds can be classified under the following heads:

I. Organic compounds not containing oxygen or halogens.
II. Compounds containing oxygen but not halogens.
III. Halogen compounds.

We shall now consider organic compounds in the above order.

I-a. *Aliphatic Compounds*

(i) Hydrocarbons.—The molecular susceptibility of the saturated hydrocarbons C_nH_{2n+2} is given exactly by the additivity formula with $\lambda = 0$ and C and H having the values given previously, i.e. $\chi_M = -[6{\cdot}25n + 3{\cdot}05(2n+2)]10^{-8}$.

(ii) Amines.—For an amine of the general type

$$C_nH_{2n+2-p}(NH_2)_p$$

the same additivity formula applies with $\lambda = 0$ and $N = -5{\cdot}8 \times 10^{-6}$.

(iii) Ethylenic Compounds.—In the case of compounds containing a double bond of the type C=C, the molecular diamagnetic susceptibility is lowered by $+5{\cdot}7 \times 10^{-6}$, giving a constitution correction of $\lambda = +5{\cdot}7 \times 10^{-6}$.

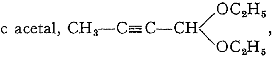
(iv) Diethylenic Compounds.—The introduction of a second double bond does not give twice the lowering of the diamagnetism of one bond. The constitution correction for diethylenic compounds of the type C=C.C=C is given by $\lambda = +11{\cdot}0 \times 10^{-6}$.

(v) Polyethylenic Compounds.—If a compound contains more than two double bonds, the third and the subsequent double bonds do not seem to have any effect on the magnetic value and λ should be counted as for diethylenic compounds.

(vi) Acetylenic Compounds.—Compounds which contain two carbon atoms joined by a triple bond of the type —C≡C— have been found to obey the additivity law with the constitutive correction $\lambda = +0{\cdot}8 \times 10^{-6}$.

Compounds of this type are: Heptine—2,

$$CH_3(CH_2)_3C{\equiv}C{-}CH_3.$$

Tetrolic acetal, 

$CH_3{-}C{\equiv}C{-}CH(OC_2H_5)_2$

, tetraethyl acetal of acetylene dialdehyde, $(C_2H_5O)_2{=}CH{-}C{\equiv}C{-}CH{=}(OC_2H_5)_2$.

Disubstituted acetylene derivatives of the type RC≡C.R′ have correction constant $\lambda = +0{\cdot}8$, while the bond R.(C=C).R occurring in ethylene derivatives requires $\lambda = +5{\cdot}7 \times 10^{-6}$.

When the triple bond occurs in a chain which also contains an aromatic nucleus the correction constant required is higher and is given by $\lambda = +1{\cdot}6 \times 10^{-6}$, which has to be added to the triple bond correction to account for the presence of the aromatic nucleus.

If two aromatic nuclei are present in the chain the above value is doubled.

In phenylacetylene, $C_6H_5{-}C{\equiv}CH$, for example, $\lambda = 1{\cdot}6 \times 10^{-6}$ accounts for the presence of the C_6H_5 group and $+0{\cdot}8 \times 10^{-6}$ for the triple bond.

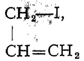
In tolane, $C_6H_5{-}C{\equiv}C{-}C_6H_5$, the two aromatic groups are to be accounted for by $\lambda = 2 \times 1{\cdot}6 \times 10^{-6}$ and the triple bond by $+0{\cdot}8 \times 10^{-6}$.

(vii) Allyl Derivatives.—The molecular susceptibilities of compounds containing an allyl double bond of the type

$$\boxed{CH_2{=}CH{-}CH_2}{-}R$$

are satisfied by taking for λ the value $+4{\cdot}7 \times 10^{-6}$.

Compounds of this type are represented by styrene, $C_6H_5{-}CH{=}CH_2$, allyl iodide

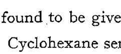


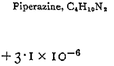
$$\begin{array}{l}CH_2{-}I,\\ |\\ CH{=}CH_2\end{array}$$

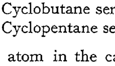
diacrolein acetylene,

$$CH_2{=}CH{-}CHOH{-}C{\equiv}C{-}CHOH{-}CH{=}CH_2$$

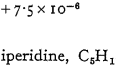
(viii) Polymethylene Derivatives.—The constitutive corrections for hydrocyclic substances and derivatives of piperidine and piperazine with the characteristic constitutions







Piperidine, $C_5H_{11}N$



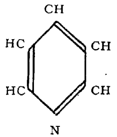
Piperazine, $C_4H_{10}N_2$

have been found to be given by

Cyclohexane series $\lambda = +3{\cdot}1 \times 10^{-6}$

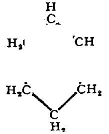
$$\left.\begin{array}{l}\text{Cyclopropane series}\\ \text{Cyclobutane series}\\ \text{Cyclopentane series}\end{array}\right\}\lambda = +7{\cdot}5 \times 10^{-6}$$

Nitrogen atom in the case of piperidine, $C_5H_{11}N$, has the value $\chi_A = -4{\cdot}8 \times 10^{-6}$, which is the same as in the case of the unreduced aromatic ring.

Pyridine, with the structural formula  appears to be an apparent exception, as in this case the value of the susceptibility obtained experimentally can be arrived at theoretically by giving $\lambda = 0$.

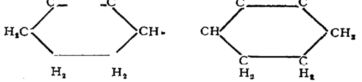
(ix) Polymethylene Derivatives exhibiting Unsaturation.*—The presence of double bonds in closed chain compounds always results in a lowering of the diamagnetism. This progressive change is clearly seen in the following compounds:

(*a*) Cyclohexene, C_6H_{10}, with the structural formula



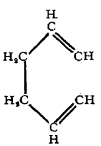
gives for the constitutive correction constant $\lambda = +7{\cdot}2 \times 10^{-6}$.

(*b*) Dicyclohexyl, C_6H_{11}—C_6H_{11}, with the structural formula



gives the constitutive correction value $\lambda = +8{\cdot}1 \times 10^{-6}$.

(*c*) Cyclohexadiene, C_6H_8, with the structural formula



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* 'Unsaturation' is here taken to mean that the compound contains a lesser number of hydrogen atoms than required for full saturation.

has two double bonds and a closed chain. The two bonds show a still further decrease in diamagnetic value given by the large +ve correction constant, $\lambda = +11{\cdot}0 \times 10^{-6}$. In general, the diamagnetic value decreases progressively as the number of double bonds is increased in a closed chain.

(x) Nitrogen Compounds.—The aliphatic compounds containing nitrogen show a number of structural peculiarities which are characterised by a different constitutive constant. The following may be particularly noted:

(*a*) Double bond between atoms of nitrogen $N{=}N$ as in azo-derivatives shows a decrease in diamagnetic value given by the constitutive correction $\lambda = +1{\cdot}9 \times 10^{-6}$.

(*b*) Double bond between atoms of carbon and nitrogen $C{=}N$: The most characteristic compounds containing this bond are oximes, $\underset{\underset{\text{NOH}}{\|}}{-\text{C}-}$, hydrazones, $\underset{\underset{\text{N.NH}_2}{\|}}{-\text{C}-}$, azomethines, $\underset{\underset{\text{N.R}}{\|}}{-\text{C}-}$

The constitution correction in these cases is found to be

$$\lambda = +8{\cdot}5 \times 10^{-6}$$

(*c*) The unsaturation between C and N, $R.C{\equiv}N$. The nitriles form the most characteristic of the above type and give for the constitutive correction $\lambda = +0{\cdot}8 \times 10^{-6}$.

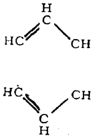
(*d*) Quadruple bond between C and N, $R.N{\equiv}C$. The characteristic compounds of this type, the carbylamines, are satisfied with the simple molecular summation of susceptibilities and consequently have no constitutive correction, $\lambda = 0$.

(*e*) Azines with the general structure $-C{=}N{-}N{=}C-$ are characterised by a large fall in diamagnetism given by the constitutive correction $\lambda = +10{\cdot}6 \times 10^{-6}$.

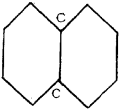
I-b. *Aromatic Compounds not containing Oxygen or Halogens*

In aromatic compounds Pascal distinguishes three types of carbon linkages which for simplicity are designated as:

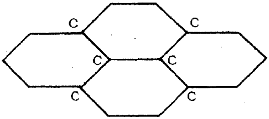
1. Mononuclear Carbon.—A carbon atom of the type that occurs in benzene or pyridine:



2. Binuclear Carbon.—A carbon atom common to two nuclei like the two central atoms of naphthalene or quinoline:



3. Trinuclear Carbon.—A carbon atom common to three nuclei as in the case of pyrene, $C_{16}H_{10}$,



The constitutive corrections for each of the above types are given by:

$\lambda =$ (i) $-0{\cdot}25 \times 10^{-6}$ for a mononuclear carbon atom.
(ii) $-3{\cdot}2 \times 10^{-6}$ for a binuclear carbon atom.
(iii) $-4{\cdot}2 \times 10^{-6}$ for a trinuclear carbon atom.

It has to be noted that the structure of the side chain attached to an aromatic nucleus exercises no constitutive influence on the nucleus. Also all the nuclei in a molecule act independently of each other.

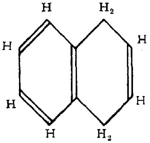
4. Nitrogen attached to Nuclear Carbon.—The constitutive correction introduced by the presence of a nitrogen atom saturating the valency of a nuclear carbon atom is found to be

$$\lambda = +1{\cdot}1 \times 10^{-6}.$$

5. Some special structures.

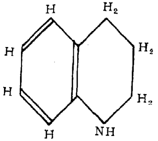
(*a*) Dihydronaphthalene, $C_{10}H_{10}$,

$$\lambda = +5{\cdot}9 \times 10^{-6}$$

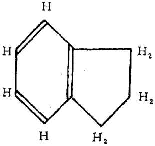


(*b*) Tetra-hydroquinoline, $C_9H_{11}N$,

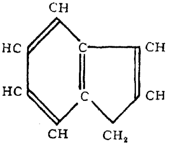
$$\lambda = +3{\cdot}4 \times 10^{-6}$$



(*c*) Hydrindene: $\lambda = +6{\cdot}55 \times 10^{-6}$



By way of illustration the susceptibility of indene may be calculated. Indene has the formula C_9H_8 with the structure



The molecular susceptibility could be calculated as

$9C = -9 \times 6{\cdot}25 = -56{\cdot}25 \times 10^{-6}$
$8H = -8 \times 3{\cdot}05 = -24{\cdot}40 \times 10^{-6}$
2 binuclear carbon atoms $= -2 \times 3{\cdot}2 = -6{\cdot}40 \times 10^{-6}$
6 mononuclear carbon atoms $= -6 \times 0{\cdot}25 = -1{\cdot}50 \times 10^{-6}$

$= -88{\cdot}55 \times 10^{-6}$

The experimental value given by Pascal is $88{\cdot}3 \times 10^{-6}$.

II-a. *Oxygen Compounds without Halogens*

The atomic susceptibility of oxygen presents an interesting case. The molecule of oxygen is paramagnetic but behaves as if it were diamagnetic or feebly paramagnetic, depending upon the configuration which it has in combination. For a simple structure not containing a tertiary or quaternary carbon or benzene nucleus Pascal differentiates three types of valency linkages, which give values for the oxygen atom according to the following rules:

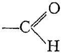
(i) An Oxygen Atom with Two Single Bonds —O—. An oxygen atom attached by single bonds to two dissimilar atoms has

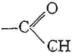
$$\chi_{-0-} = -4{\cdot}8 \times 10^{-6}$$

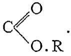
e.g. the normal alcohols R—O—H where the oxygen atom is singly linked to one carbon and one hydrogen atom.

(ii) An Oxygen Atom with a Double Bond C=O. An oxygen atom attached by a double bond to one atom of carbon which has no other oxygen atom attached to it behaves as a feeble paramagnetic, with atomic susceptibility

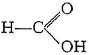
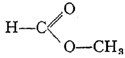
$$\chi_{=0} = +1{\cdot}8 \times 10^{-6}$$

e.g. the aldehydes 

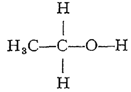
or ketones 

(iii) An Oxygen Atom with a Double Bond in a Carboxyl Type of Group  . An oxygen atom attached by a double bond to a carbon atom which has another atom of oxygen attached to it by a single bond has the atomic susceptibility

$$\chi_{=0'} = -3{\cdot}5 \times 10^{-6}$$

In such compounds the other atom of oxygen will have a value $\chi_{-0-} = -4{\cdot}8 \times 10^{-6}$ according to rule (i) above. Examples of this type are the various organic acids, e.g. formic acid,  or their esters like methyl formate, 

A few examples can be given to make Pascal's procedure clear. Taking the case of ethyl alcohol with the formula



$$H_3C\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{—}O\text{—}H$$

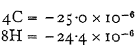
it is seen that the oxygen atom is attached to one carbon and one hydrogen atom, and as such its atomic susceptibility should be $\chi_{-O-} = -4{\cdot}8 \times 10^{-6}$ according to (i) above. The value for the compound is then obtained by addition as follows:

$$\begin{aligned} 2C &= -12{\cdot}5 \times 10^{-6} \\ 6H &= -18{\cdot}3 \times 10^{-6} \\ \text{—}O\text{—} &= -4{\cdot}8 \times 10^{-6} \\ \hline \chi_M &= -35{\cdot}6 \times 10^{-6} \end{aligned}$$

Pascal's experimental value for ethyl alcohol is

$$\chi_M = -35{\cdot}7 \times 10^{-6}$$

In the case of a compound like methylethylketone which has the graphic formula



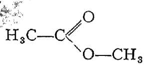
the oxygen atom is attached by a double bond to the carbon atom. No other bond of this C atom is linked to an O atom. The oxygen atom should, therefore, have the value $+1{\cdot}8 \times 10^{-6}$, and the molecular susceptibility of the compound can thus be calculated as before:

$$\begin{aligned} 4C &= -25{\cdot}0 \times 10^{-6} \\ 8H &= -24{\cdot}4 \times 10^{-6} \\ =O &= +1{\cdot}8 \times 10^{-6} \\ \chi_M &= -47{\cdot}6 \times 10^{-6} \end{aligned}$$

Pascal's experimental value for methylethylketone is

$$\chi_M = -47{\cdot}5 \times 10^{-6}$$

Similarly, in the case of a compound like methyl acetate, with the graphic formula



we notice that there are two oxygen atoms in the molecule, one of which is attached to the central carbon atom with a double bond while the other is linked to it with one single bond. In this case the oxygen atom with the double bond will have a value $-3{\cdot}5 \times 10^{-6}$ and the other oxygen atom with the single bond will take the value $-4{\cdot}8 \times 10^{-6}$, as in the case of a hydroxyl. The molecular susceptibility will accordingly be calculated as below:

$$\begin{aligned} 3C &= -18{\cdot}75 \times 10^{-6} \\ 6H &= -18{\cdot}30 \times 10^{-6} \\ =O' &= -\ \ 3{\cdot}50 \times 10^{-6} \\ -O- &= -\ \ 4{\cdot}80 \times 10^{-6} \end{aligned}$$

$$\chi_M = -45{\cdot}35 \times 10^{-6}$$

Pascal's experimental value for methyl acetate is

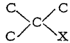
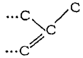
$$\chi_M = -45{\cdot}5 \times 10^{-6}$$

(iv) Oxygen Compounds containing an Ethylene Bond.—In compounds containing oxygen the presence of a double bond has always a marked effect in lowering the diamagnetism. The position of oxygen in the structural formula, with respect to the position of other carbon atoms in the molecule, also exercises profound influence. In order to correct for these structural effects Pascal gave a set of empirical rules.

When the functional group containing a substituted oxygen atom is in any of the positions given in the table below with respect to tertiary * or quaternary C atom the constitution constant λ will have the respective values indicated.

---

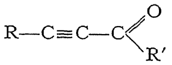
* A tertiary or quaternary carbon atom is defined by Pascal as an atom of which 3 or 4 valencies, respectively, are saturated by atoms of carbon, whatever be the number of the latter. Tertiary or quaternary C atoms can be designated by the symbols C_3^{α}, C_3^{β}, C_3^{γ}, . . . and C_4^{α}, C_4^{β}, C_4^{γ}, . . ., etc., respectively, where α, β, γ, etc., denote their position with respect to the oxygen group. This notation, though not common to organic chemistry, has been retained here because of its simplicity and ease of expression.

Position	Tertiary Carbon, C_3 	Quaternary Carbon, C_4 
$\alpha, \gamma, \delta, \epsilon$	$-1{\cdot}35 \times 10^{-6}$	$-1{\cdot}6 \times 10^{-6}$
β	$-0{\cdot}5 \times 10^{-6}$	$-0{\cdot}5 \times 10^{-6}$
ϕ, η	$-0{\cdot}8 \times 10^{-6}$	$-1{\cdot}0 \times 10^{-6}$
θ, ι	0	0

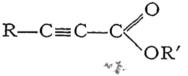
NOTE.—Polymethylene derivatives containing oxygen and having no side chain of the cyclohexane structure should be regarded as saturated normal aliphatic compounds.

Similarly saturated closed chains containing oxygen as a fundamental element, e.g. paraldehyde, tetrahydrofurfurane, containing no side chain behave similarly to open-chain aliphatic compounds.

(v) The Triple Bond with $\mathrm{C}\begin{smallmatrix}\mathrm{O}\\ \mathrm{R'}\end{smallmatrix}$ and $\mathrm{C}\begin{smallmatrix}\mathrm{O}\\ \mathrm{OR'}\end{smallmatrix}$ Groups.—The corrective constant for the presence of the groups of the following general type

(*a*) 

$R{-}C{\equiv}C{-}C\begin{smallmatrix}O\\ R'\end{smallmatrix}$

(*b*) 

$R{-}C{\equiv}C{-}C\begin{smallmatrix}O\\ OR'\end{smallmatrix}$

is given by

$$\lambda = +0{\cdot}85 \times 10^{-6}$$

Compounds of this type are: ethyl amyl propiolate,

$$C_5H_{11}{-}C{\equiv}C{-}COO.C_2H_5$$

and butryl phenylacetylene,

$$C_3H_7{-}CO{-}C{\equiv}C{-}C_6H_5.$$

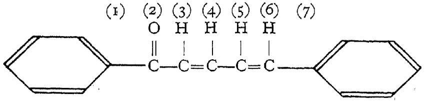
NOTE.—*The triple bond in acetylene derivatives containing oxygen*: The triple bond forms a magnetic screen between the two portions of the molecule which it joins, similarly to an aromatic nucleus which establishes the most perfect magnetic independence between the different side branches. Thus in any calculation in which the influence of oxygenated groups is to be taken into account due to the presence of tertiary or quaternary

C atoms the two sides of the triple bond have to be treated and allowed for as independent of each other.

(vi) Aromatic Oxygen Compounds.—For aromatic compounds a mononuclear carbon should be considered as tertiary if it does not carry the carbon side chain. If it carries a carbon side chain it should be regarded as a quaternary.

An Exception.—An important exception may be noted: when an open-chain carbon contains an oxygen attached to two identical groups or an oxycarbon group attached to two similar radicals, then owing to the symmetry of the molecule the constitution corrections for the tertiary and quaternary carbons cancel themselves. Examples of this type are found in diphenyl ether, benzophenone, xanthone.

Examples.—It would be instructive to illustrate the foregoing rules by a few examples. We shall first take diphenylpentadienone:



The molecular susceptibility is added as follows:

17 atoms of carbon	$-17\times6{\cdot}25=$	$-106{\cdot}25\times10^{-6}$
14 atoms of hydrogen	$-14\times3{\cdot}05=$	$-\ 42{\cdot}70\times10^{-6}$
1 atom of oxygen	$=0$	$=+\ 1{\cdot}80\times10^{-6}$
2 double bonds		$=+\ 11{\cdot}00\times10^{-6}$
12 mononuclear carbons	$-12\times0{\cdot}25=$	$-\ 3{\cdot}00\times10^{-6}$
	Total	$-139{\cdot}15\times10^{-6}$

As the compound contains one CO group the influence of the tertiary and quaternary C atoms upon it can be calculated as below:

Carbons	(1)	(3)	(4)	(5)	(6)	(7)
	C_4^{α}	C_3^{α}	C_3^{β}	C_3^{γ}	C_3^{δ}	C_4^{ϵ}
$\Sigma\lambda=$	$-1{\cdot}6$	$-1{\cdot}35$	$-0{\cdot}5$	$-1{\cdot}35$	$-1{\cdot}35$	$-1{\cdot}6$

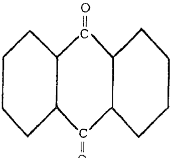
$= -7{\cdot}75\times10^{-6}$

The molecular susceptibility is therefore equal to

$$\chi_M = -(139{\cdot}15+7{\cdot}75)\times10^{-6} = -146{\cdot}9\times10^{-6}$$

Pascal's experimental value $= 146{\cdot}2\times10^{-6}$.

Anthraquinone, $C_{14}H_8O_2$,



offers another interesting example. If this compound is considered as consisting of two benzene nuclei attached to one another by two aliphatic chains, then the calculated value on the basis of symmetrical oxygen groups comes out to be $\chi = -111{\cdot}3 \times 10^{-6}$ while the experimental value is $-124{\cdot}6 \times 10^{-6}$. The large difference between the calculated and experimental values is clearly accounted for when anthraquinone is considered as possessing anthracene structure. Anthracene contains 4 binuclear C atoms and 10 mononuclear C atoms, and two of these in anthraquinone formation become attached to oxygen. There is no constitutive correction for oxygen due to symmetry. Thus we calculate as below:

$\Sigma\alpha\chi = 14$ carbon + 8 hydrogen + 2 oxygen atoms with double bond

$$= -\underset{14\ \mathrm{C}}{(14 \times 6{\cdot}25)} - \underset{8\ \mathrm{H}}{(8 \times 3{\cdot}05)} + \underset{2\ =\mathrm{O}}{(2 \times 1{\cdot}8)}$$

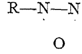
$\Sigma\lambda = 8$ mononuclear carbon atoms + 4 binuclear carbon atoms + no influence upon oxygen

$$= -(8 \times 0{\cdot}25 + 4 \times 3{\cdot}2) = -14{\cdot}8 \times 10^{-6}$$

Hence $\chi_M = 123{\cdot}1 \times 10^{-6}$.

The agreement with the experimental value is very satisfactory.

II-b. *Compounds containing Oxygen and Nitrogen*



(i) Azoxy Compounds of the type $R{-}N{-}\underset{\displaystyle O}{N}.R.$* Nitrogen

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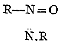


* The recent view about the structure of azoxy compounds gives them the unsymmetrical structure of the type

$$\begin{array}{c} R{-}N{=}O \\ \ddot{N}.R \end{array}$$

behaves towards O like a tertiary carbon entering into the constitution of the functional group. From the magnetic point of view the N of an azoxy compound can be regarded as similar to an atom of C with its one valency saturated by a hydrocarbon radical of normal structure.

(ii) Nitroso-derivatives of the type $-N=O$. The structural constants of the group can be calculated by considering the nitrogen of the functional group as similar to the radical $>C-R$ and consequently the group $-N=O$ to the group $-\underset{\substack{|\\ R}}{C}=O$.

(iii) Amides and Imides.—In the case of monoamides the atomic susceptibility of nitrogen is to be counted as

$$\chi = -1{\cdot}6 \times 10^{-6}$$

and in diamides and the imides

$$\chi = -2{\cdot}2 \times 10^{-6}$$

NOTE.—Nitrogen, when it occurs in compounds along with oxygen, behaves in an exceptional manner and seems to disobey Pascal's additivity principles in several cases.

III. *Halogen Compounds*

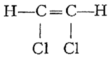
(i) Monohalogen Derivatives.—The monohalogen derivatives show the following constitutive corrections:

	$\lambda \times 10^6$
Cl	$+3{\cdot}2$
Br, I . . .	$+4{\cdot}25$

(ii) Dihalogen Derivatives.—In compounds like ethylene halides and amylene halides which are derived from the saturation of ethylenic hydrocarbons the constant was found to have the following values:

	$\lambda \times 10^6$
Dichloro derivatives	$+4{\cdot}5$
Dibromo derivatives	$+6{\cdot}5$

It will be seen that in compounds of the above type, viz. $-C_2H_2Cl_2-$, there is a potential possibility of the formation of a hydrogen halide by the combination of the adjacent H and Cl atoms:

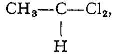


$$\underset{\text{Cl}}{\underset{|}{\text{H—C}}}=\underset{\text{Cl}}{\underset{|}{\text{C—H}}}$$

According to Pascal, the decrease in the diamagnetism of an ethylenic compound is greatly influenced by the existence of a double bond. He believed that in all cases of oxygenated or halogenated substances, where by the loss of the elements of water or hydrogen halide there was a potential possibility of an ethylenic compound being formed, a similar decrease of diamagnetism should be expected.

(iii) Two Halogen Atoms attached to the same C Atom.—In compounds where two halogens are attached to the same atom of carbon the decrease of diamagnetism is still more marked. Here we may distinguish two slightly different types. In tetrachloroethylene, $CCl_2{=}CCl_2$, for example, we have no H atoms present and so the diamagnetic decrease is simply due to the mutual interaction of the Cl atoms. The theoretical and calculated values differ by $2{\cdot}9 \times 10^{-6}$ in this case, from which we have for each Cl_2 group

$$\lambda = 1{\cdot}5 \times 10^{-6}$$

In the other type, the dihalogen derivatives of aldehydes for example, the influence of the presence of H in the same group as Cl is clearly seen. With ethylidene chloride,  $CH_3\text{—}\underset{\text{H}}{\underset{|}{\text{C}}}\text{—}Cl_2$, the difference between the calculated and experimental values is $6{\cdot}7 \times 10^{-6}$ in which λ for $Cl_2 = 1{\cdot}5 \times 10^{-6}$, giving the constant of correction for the presence of H in the group of the same order of magnitude as given by the dichloro derivatives

$$\lambda = 5{\cdot}2 \times 10^{-6}$$

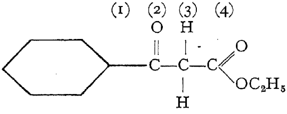
(iv) Aromatic Nucleus.—If, however, the group $CHCl_2$ is attached to a benzene nucleus in which the potential possibility of hydrogen halide formation is very much less than in the case of the aliphatic compounds, the value for λ is also much smaller.

As in the case of certain nitrogen compounds it should also be remarked here that the polyhalogen derivatives behave in a very exceptional manner.

The study of tautomeric compounds offers an interesting field for the application of the additivity principles. It is possible in this manner to calculate the theoretical values for the two different tautomeric forms. By comparing these values with the experimentally determined value it is possible to calculate the relative amount in which the two tautomers exist in the compound. We consider, for example, tautomeric compounds such as *β*-ketonic esters and *β*-diketones. For ethyl benzoylacetate with the two possible formulae

$$C_6H_5COCH_2COOC_2H_5 \quad \text{or} \quad C_6H_5C(OH){=}CHCOOC_2H_5$$

the ketonic structure is written as



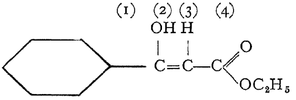
the molecular susceptibility of which is given by

$$\underset{-68{\cdot}75}{[11C]}+\underset{-36{\cdot}6}{[12H]}+\underset{+1{\cdot}8}{[=O]}+\underset{-3{\cdot}5}{[=O']}+\underset{-4{\cdot}8}{[-O-]}+\lambda=-111{\cdot}85\times10^{-6}+\Sigma\lambda$$

To find $\Sigma\lambda$ it will be noticed that the compound contains (*a*) one benzene nucleus (correction constant $-1{\cdot}5\times10^{-6}$); (*b*) a quaternary carbon atom at position marked (1) which occupies (i) α-position with respect to the CO group needing a correction constant $=-1{\cdot}6\times10^{-6}$, and (ii) β-position with respect to the $CO_2C_2H_5$ group needing a correction constant $=-1{\cdot}6\times10^{-6}$.

Hence $\Sigma\lambda=-4{\cdot}7\times10^{-6}$, giving for χ_M the calculated value $116{\cdot}5\times10^{-6}$.

The enolic structure of the compound is written as



the molecular susceptibility of which is added as below:

$$\underset{-68{\cdot}75}{[11C]}+\underset{-36{\cdot}6}{[12H]}+\underset{-4{\cdot}8}{[-O-]}+\underset{-3{\cdot}5}{[=O']}+\underset{-4{\cdot}8}{[-O-]}=-118{\cdot}45\times10^{-6}$$

To evaluate $\Sigma\lambda$ it will be noticed that the compound has two oxygenated functional groups C(OH) and $CO_2C_2H_5$ and contains

(*a*) one benzene nucleus $(\lambda = -1{\cdot}5 \times 10^{-6})$;
(*b*) one double bond with correction constant $= +5{\cdot}7 \times 10^{-6}$;
(*c*) a quaternary C atom at position marked (1) which is in (i) α-position with respect to the C(OH) group $(\lambda = -1{\cdot}6 \times 10^{-6})$, (ii) γ-position with respect to the $CO_2C_2H_5$ group $(\lambda = -1{\cdot}6 \times 10^{-6})$;
(*d*) a tertiary C atom at position marked (3) which is in (i) α-position with respect to C(OH) group $(\lambda = -1{\cdot}35 \times 10^{-6})$, and (ii) α-position with respect to the $CO_2C_2H_5$ group (correction constant $\lambda = -1{\cdot}35 \times 10^{-6}$);
(*e*) a tertiary C atom in position marked (2) which is in β-position with respect to the $CO_2C_2H_5$ group (correction $\lambda = -0{\cdot}5 \times 10^{-6}$).

Hence $\chi_M = (-118{\cdot}45 - 2{\cdot}2) \times 10^{-6} = -120{\cdot}65 \times 10^{-6}$.

Therefore this result supports the fact that ethyl benzoylacetate is mostly enolic in its chemical reactions.

TABLE IV

SUSCEPTIBILITY CONSTANTS. $\chi_A \times 10^6$

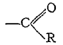
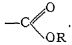
Element	Pascal's Value	Corrected Value
H	−3·05	−2·93
C	−6·25	−6·00
N, Open chain	−5·8	−5·57
Closed chain	−4·8	−4·61
Monoamides	−1·6	−1·54
Diamides and imides	−2·2	−2·11
O, R—O—R′	−4·8	−4·61
	+1·8	+1·73
	−3·5	−3·36
F	−11·98	−11·5
Cl	−20·95	−20·11
Br	−31·92	−30·64
I	−46·5	−44·64
S	−15·6	−14·98
Se	−24·0	−23·04
Te	−38·9	−37·34
P	−27·4	−26·30
Sb	−77·5	−74·40
Bi	−189·6	−182·02

TABLE V

CONSTITUTIVE CORRECTION CONSTANTS. $\lambda \times 10^6$

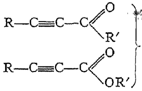
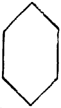
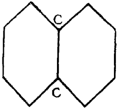
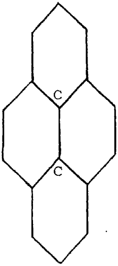
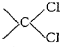
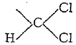
	Pascal's Value	Corrected Value
$-\overset{\vert}{C}=\overset{\vert}{C}-$, ethylenic linkage .	+5·7	+5·47
$-\overset{\vert}{C}=\overset{\vert}{C}.\overset{\vert}{C}=\overset{\vert}{C}-$, diethylenic linkage	+11·0	+10·56
$-C\equiv C-$, acetylenic linkage .	+0·8	+0·77
$AR-C\equiv C-$	(1·6+0·8) = 2·4	(1·54+0·77) = +2·31
$AR-C\equiv C-AR$ . . .	(1·6 × 2+0·8) =4·0	(1·54 × 2+0·77) = +3·85
$CH_2=CH-CH_2-$, allyl linkage .	+4·7	+4·51
Cyclohexane series . . .	+3·1	+2·98
Cyclopropane series Cyclobutane series Cyclopentane series . .	+7·5	+7·20
C_6H_{10}, cyclohexene . . .	+7·2	+6·91
$C_6H_{11}-C_6H_{11}$, dicyclohexyl .	+8·1	+7·78
C_6H_8, cyclohexadiene . . .	+11·0	+10·56
$-N=N-$, azo type . . .	+1·9	+1·82
$\underset{\underset{N-R}{\Vert}}{-C-}$	+8·5	+8·16
$RC\equiv N$	+0·8	+0·77
$RN\equiv C$	+0·0	+0·00
$-\overset{\vert}{C}=N-N=\overset{\vert}{C}-$ (azines) . .	+10·6	+10·18
 $R-C\equiv C-C\begin{smallmatrix}\nearrow O\\ \searrow R'\end{smallmatrix}$ $R-C\equiv C-C\begin{smallmatrix}\nearrow O\\ \searrow OR'\end{smallmatrix}$ . .	+0·85	+0·82
Mononuclear C 	−0·25	−0·24
Binuclear C  C C	−3·2	−3·07

TABLE V (*continued*)

	Pascal's Value	Corrected Value
Trinuclear C 	$-4·2$	$-4·03$
—N═O	$+1·8$	$+1·73$
—C—Cl mono-halogen derivatives	$+3·2$	$+3·07$
—C—Br —C—I ,, ,,	$+4·25$	$+4·08$
Cl—C—C—Cl dichloro derivatives	$+4·5$	$+4·32$
Br—C—C—Br dibromo derivatives	$+6·5$	$+6·24$
	$+1·5$	$+1·44$
	$(1·5+5·2)$ $=+6·7$	$(1·44+4·99)$ $=+6·43$
C_3 in α, γ, δ, ϵ position	$-1·35$	$-1·29$
C_4 in α, γ, δ, ϵ position	$-1·60$	$-1·54$
C_3 and C_4 in β position	$-0·5$	$-0·48$
C_3 in ϕ, η position	$-0·8$	$-0·77$
C_4 in ϕ, η position	$-1·0$	$-0·96$
C_3 and C_4 in θ, i position	0	0

It is impossible to deal with all the compounds which Pascal studied. The conclusions arrived at by Pascal are occasionally faulty and the values of the susceptibility in some cases are also doubtful. For the sake of ready reference the susceptibility constants determined from Pascal's work and corrected for the susceptibility of water $-0{\cdot}72 \times 10^{-6}$ as against $-0{\cdot}75 \times 10^{-6}$ are gathered together in the preceding tables.

Pascal employed magnetic susceptibility as a physical property capable of yielding successful clues to chemical constitution on the same lines as any other physical property. The electronic theories of matter were then in their infancy and Pascal could hardly have realised that a day would come when magnetism and spectroscopy would furnish the two most successful and fruitful avenues of approach to the secret portals of the atom. The important relationship between these two branches of physics has necessitated the inclusion of the next chapter.

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CHAPTER V

AN INTRODUCTION TO SPECTROSCOPY AND ATOMIC STRUCTURE

MANY ingenious attempts have been made in recent years to account for the magnetic behaviour of the atom on the basis of the spectroscopic properties. There appears to be no doubt that the future progress of the atomic theories will be connected more and more intimately with the development of the spectroscopic theory in relation to the magnetic properties of the atoms and molecules. The treatment of spectroscopy given in this chapter is necessarily brief and the selection has been restricted to such topics as have a bearing on the theories of magnetochemistry.

1. THE BOHR THEORY OF THE HYDROGEN ATOM

Bohr's theory supplied the spectroscopic counterpart of the quantum concepts of Max Planck. Like Planck's theory it was based upon certain fundamental postulates which expressed experimental truths without any reference to a detailed mechanism of the internal processes. The immediate success of Bohr's theory was in fact due to the excellent explanation it gave of a vast amount of experimental facts. The atomic model proposed by Bohr is based on the assumption that electrons and nuclei inside the atom maintain their independent existence as point charges in an inverse square field of force obeying the laws of Newtonian mechanics. Bohr's model for the simplest atom, that of hydrogen, consists of a single electron of mass m revolving in a circle of radius a around a positive nucleus of charge $+Ze$. The nucleus is considered so heavy in comparison to the electron that it is assumed to be at rest. In a hydrogen atom the nucleus carries a single positive charge and so $Z=1$; for a singly ionised He atom $Z=2$. For dynamic equilibrium the electrostatic attraction directed towards the nucleus is equal to the centrifugal force. This is expressed by the relation

$$\frac{Ze^2}{a^2}=\frac{mv^2}{a} \quad . \quad . \quad . \quad . \quad (1)$$

where v is the velocity of the revolving electron. The kinetic energy of the electron is $\frac{1}{2}mv^2$ and the potential energy is $-\frac{Ze^2}{a}$, assuming that the energy is zero when the electron is at infinity. The total energy W is therefore given by

$$W = \tfrac{1}{2}mv^2 - \frac{Ze^2}{a} \quad . \quad . \quad . \quad . \quad (2)$$

or substituting from (1), we get

$$W = \frac{Ze^2}{2a} - \frac{Ze^2}{a} = -\frac{Ze^2}{2a}$$

Also, the revolving electron possesses an angular momentum about the nucleus given by

$$p = mva \quad . \quad . \quad . \quad . \quad (3)$$

Eliminating v and a from equation (2), by equations (1) and (3),

$$W = -\frac{me^4Z^2}{2p^2} \quad . \quad . \quad . \quad (4)$$

We here introduce a *quantum condition* prescribed by Bohr, that only those orbits are 'allowed' in which the angular momentum is an integral multiple of $\frac{h}{2\pi}$ where h is the well-known Planck's constant. That is,

$$2\pi p = nh$$

where n is an integer.

The total energy in equation (4) can, therefore, only assume the values given by

$$W_n = -\frac{2\pi^2me^4Z^2}{n^2h^2} \qquad n = 1, 2, \ldots \qquad (5)$$

The different W_n values obtained by putting $n = 1, 2, \ldots$, define the different *stationary states* which the atom can assume, and further in these stationary states the atom does not radiate any energy. Bohr now introduced a further *frequency condition* that the emission of radiation by an atom or molecule occurs only during a transition from a stationary state of energy W_{n_2} to another having a lower energy level W_{n_1}, and the quantum of energy thus emitted consists of a nearly monochromatic wave train. Thus, for a transition from the orbit $n = n_2$ to $n = n_1$ (where $n_2 > n_1$), the emitted energy is given by

$$h\bar{\nu} = W_{n_2} - W_{n_1} = \frac{2\pi^2 me^4 Z^2}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or the emitted monochromatic frequency is given by

$$\bar{\nu} = \frac{W_{n_2} - W_{n_1}}{} = \frac{2\pi^2 me^4 Z^2}{}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad . \quad . \quad (6)$$

It is customary in spectroscopic practice to use the reciprocal of wave-length or the wave-numbers ν instead of frequency $\bar{\nu}$, and consequently we have for equation (6)

$$\nu = \frac{2\pi^2 me^4 Z^2}{h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

The constant $\frac{2\pi^2 me^4}{h^3 c}$ called *Rydberg's constant* is usually denoted by the letter R. The formula for hydrogen can consequently be written as

$$\nu = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad n_1 = 1, 2, 3, \ldots \quad . \quad . \quad (7)$$

This formula, based on the simplest of assumptions, accurately predicted the Lyman, Balmer and Paschen series of lines for hydrogen.

2. GENERALISED BOHR THEORY

It is obvious that the simple circular model discussed above would be wholly inadequate to explain the more complicated atomic structures. The more elaborate generalisations have been given by Wilson, Sommerfeld and others.

To represent the general quantum conditions Sommerfeld makes use of the generalised co-ordinates in a periodic system having n degrees of freedom. In such a system q co-ordinates are selected such that each generalised momentum p_k is a function only of the corresponding q_k. The stationary states are then determined by the condition

$$\oint p_k dq_k = n_k h \quad . \quad . \quad . \quad . \quad (8)$$

where n_k is an integer and the integration extends over a complete cycle of the variable q_k. By putting $n_k = 1, 2, \ldots$, in turn we fix the first, second, . . ., quantised phase-orbits of the kth degree of freedom.

3. ELLIPTICAL ORBITS—THE AZIMUTHAL QUANTUM NUMBER

Ordinarily, the generalised equation (8) gives an electron revolving in an elliptical orbit. While in the circular case any orbit could be completely defined by taking only one variable term n, in the case of an elliptical orbit two such numbers are required to fix any state. It was found that the possible eccentricities of the ellipse could be determined by taking a subsidiary quantum number k, which should not be greater than n, the principal quantum number. k was called the azimuthal quantum number. The ratio of k to n fixes the ratio of the minor to the major axis of the orbit. A particular orbit characterised by quantum numbers n, k, could therefore be referred to as an n_k orbit. It should be noted that the energy of an orbit depends only on the principal quantum number n and not on k, i.e. it is a function only of the major axis of the ellipse and not of its eccentricity.

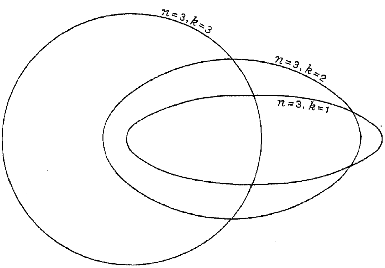

FIG. 26.—Bohr orbits for $n=3$, $k=1$, 2 and 3.

According to Bohr's conditions k can assume only integral values. Thus for orbits with $n=3$, (say) k can have the possible values $k=1$, 2, 3, giving the three corresponding orbits 3_1, 3_2 and 3_3. In the 3_1 orbit the minor axis is 1/3 of the major axis; in 3_2 the minor axis is 2/3 of the major axis and in 3_3 the major and minor axes will be equal, and the orbit will be circular.

The orbit corresponding to the normal state of the hydrogen atom is that with $n=1$, $k=1$. It is a circular orbit with radius $a_0=0{\cdot}5284\times10^{-8}$ cm. (for $Z=1$). In ionised helium (He^+) the radius of this orbit is $\frac{a_0}{2}$. The quantum number k has been replaced in the new quantum mechanics by l, which is numerically equal to $(k-1)$.

4. ENERGY STATES AND SPECTRAL TERMS

The energy states of an atom (or ion) are determined from the frequencies of the observed spectral lines. According to equation (6) the frequency of an emitted spectral line is given by

$$\bar{\nu}=\frac{W_1-W_2}{h}\ \text{sec}^{-1} \qquad . \quad . \quad . \quad (9)$$

and this is easily seen to be the difference of two terms $\frac{W_1}{h}$ and $\frac{W_2}{h}$. The analysis of the structure of a spectrum consists primarily in fixing the values of the energy states. The energy states, as usually expressed in units of wave-numbers (i.e. the number of waves per cm.), are generally called the *terms* and their values the *term values*. Once the term values for an atom have been determined it is possible to deduce the wavelengths of other spectral lines from them by taking the various term differences. In general, combinations between all the terms are not possible. Only certain combinations are *allowed*, others are *forbidden*. The rules governing these transitions are known as *Selection Rules*.

5. THE SPIN OF THE ELECTRON

In the simple orbital theory considered above, deductions have been made on the assumption that the electron possesses only the angular momentum due to the orbital motion. This was the basis of the older quantum theory, but it was shown by Uhlenbeck and Goudsmit in 1926 that the revolving electron itself possessed an 'intrinsic' angular momentum due to its spin about its own axis. Experiments have shown that the intrinsic angular momentum of the electron is $\frac{1}{2}\frac{h}{2\pi}$ and its magnetic moment is $\frac{h}{2\pi}.\frac{e}{2m_0c}$.

6. THE QUANTUM NUMBERS

Each electron in an atom can be assigned four quantum numbers, namely:

n, the principal quantum number, which takes integral values and is related to the size of the orbit in the Bohr model;

l, the angular momentum of the orbital motion, measured in terms of the quantum units $\frac{h}{2\pi}$. l can only take integral values and equals $(k-1)$ of the older theory;

s, the spin quantum number. It is measured in the terms of the quantum units $\frac{h}{2\pi}$, i.e. $\frac{sh}{2\pi}$ is the angular momentum of the electron spinning about its own axis. For every single electron $s=1/2$.

j, the resultant angular momentum is defined as the vector sum of l and s; j can take the possible values

$$l+s,\ l+s-1,\ \ldots,\ |\,l-s\,|$$

which for a system having one electron reduces to $l-1/2$ and $l+1/2$. Where $l=0$, $j=1/2$ is the only possible value. It is also measured in units of $\frac{h}{2\pi}$.

In the presence of a weak magnetic field the vector j precesses about the direction of the lines of force. The atom becomes space quantised and the component of j in the direction of the field is called the magnetic quantum number. On the other hand, in a strong magnetic field, the coupling of the j and s vectors is broken down and each of these vectors becomes independently space-quantised, so that, in the presence of a strong magnetic field, each electron becomes definitely characterised by the five quantum numbers: *

$$n = 1,\ 2,\ 3,\ \ldots$$
$$l = 0,\ 1,\ 2,\ \ldots,\ n-1 \text{ (vector)}$$
$$s = 1/2 \text{ (vector)}$$
$$m_l = -l,\ -l+1,\ \ldots,\ 0,\ \ldots,\ l-1,\ l.$$
$$m_s = -1/2,\ +1/2.$$

---

* According to the notation recommended by the American Committee of Spectroscopists (*Phys. Rev.* **33**, 900, 1929), the small letters n, l, s, j, m are used for the quantum numbers of an electron and the capital letters L, S, J, M to designate the quantum numbers of a term (or level) of an atom (or ion).

H

7. THE VECTORS $\mathbf{s}$ AND $\mathbf{l}$

The orbital momentum $\mathbf{l}$* and the spin moment $\mathbf{s}$ have been both defined to be vectors. The resultant of $\mathbf{l}$ and $\mathbf{s}$ gives for the angular momentum the vector $\mathbf{j}$. The vectors can be compounded by the graphical method of triangle of forces by taking the sides proportional to the magnitudes of the quantities.

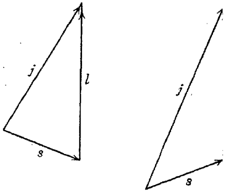

FIG. 27.—Composition of vectors $\mathbf{s}$ and $\mathbf{l}$ to form the resultant $\mathbf{j}$. The magnitudes of vectors are $\sqrt{s(s+1)}$, $\sqrt{l(l+1)}$, and $\sqrt{j(j+1)}$.

If the magnitudes of the vectors $\mathbf{s}$, $\mathbf{l}$ and $\mathbf{j}$ are taken as s, l and j respectively, we obtain from the application of the trigonometrical relation connecting the three sides of a triangle the relation

$$\cos(\mathbf{sl}) = \frac{j^2 - s^2 - l^2}{2sl}$$

The new quantum mechanics has introduced corrections in the magnitude of the quantum vectors by replacing l^2 by $l(l+1)$, j^2 by $j(j+1)$ and s^2 by $s(s+1)$; the equation given above accordingly becomes

$$\cos(\mathbf{sl}) = \frac{j(j+1) - s(s+1) - l(l+1)}{2sl} \qquad (10)$$

This equation enables the calculation of the angle between the orbital and spin moments of an electron.

8. ELECTRON CONFIGURATIONS AND NOTATION

For an atom having several electrons each of the electrons is characterised by n, l values. It is convenient to use special symbols to denote the values of n and l. This is done by using a whole number to represent the principal quantum number n, and followed by the letters s, p, d, . . ., etc., to denote the values for $l = 0, 1, 2$, etc.

Thus the symbols		s	p	d	f	g	h	i
stand for	$l =$	0	1	2	3	4	5	6 etc.

---

* The usual custom of indicating vector quantities by bold face type has been adopted here.

When several electrons in an atom have the same value for n and l their number is indicated by a superscript, for example $2p^6$ will mean 6 electrons with $n=2$, $l=1$. For atoms containing many electrons it is usual to give the symbols only for the outermost electrons, as the inner groups do not contribute to the optical spectra.

9. ODD AND EVEN TERMS—SELECTION RULE FOR l

The energy levels of each spectrum can be divided into two groups: even terms and odd terms. Even terms are those in which the arithmetical sum of all l's of the electrons is even; odd terms are those in which the sum is odd. The spectroscopic symbols for odd levels are distinguished by the sign $^\circ$ at the upper right side and term value is printed in italics. The odd and even terms are distinguished by the fact that transitions can occur only between an odd state and an even state—and not between two odd or two even states. Transitions between two odd or two even terms become possible under the perturbing influence of electric fields—either external or due to neighbouring atoms. Such transitions are called *forbidden*.

The same fact is stated in the form of a selection rule for l: when there is a transition of only one electron, only those combinations occur for which the quantum number l changes by $+1$ or -1.

10. SELECTION RULE FOR J

It was found empirically that the total angular momentum quantum number J can change during a transition only by 0 or ± 1. In addition, the transition $J=0 \rightarrow J=0$ is forbidden. The selection rule for J is not rendered invalid by perturbing external electric fields, as is the case for l. It is, however, violated by external magnetic fields.

11. RUSSELL-SAUNDERS COUPLING

In an atom which contains several electrons outside of the completed groups or sub-groups (the so-called valency electrons) each of the electrons is represented by means of an orbital moment vector $\boldsymbol{l}_i$ and a spin moment vector $\boldsymbol{s}_i$ (for the ith electron) together with the resultant vector $\boldsymbol{j}_i$ formed from them. When there are more than one outside electrons the problem arises as to how the $\boldsymbol{l}$ and $\boldsymbol{s}$ vectors of the electrons are coupled to give the resultant. There are several possible ways of coupling, but two of these may be considered.

(i) One possibility is that the $\boldsymbol{s}_i$ vectors of all the electrons combine to form a resultant $\boldsymbol{S}$, and independently the $\boldsymbol{l}_i$ vectors form a resultant $\boldsymbol{L}$. The two resultants $\boldsymbol{S}$ and $\boldsymbol{L}$ then further combine vectorially to form the total moment $\boldsymbol{J}$. Thus we may write

$$[(\boldsymbol{s}_1\boldsymbol{s}_2\boldsymbol{s}_3, \ldots)(\boldsymbol{l}_1\boldsymbol{l}_2\boldsymbol{l}_3, \ldots)] = (\boldsymbol{S}.\boldsymbol{L}) = \boldsymbol{J}$$

(ii) Another possibility is that for each electron (ith electron) its spin moment $\boldsymbol{s}_i$ still maintains coupling with its orbital moment $\boldsymbol{l}_i$, and that this coupling is not broken by interaction with other electrons. In this way each electron has its own resultant $\boldsymbol{j}_i$ and all the $\boldsymbol{j}_i$'s then combine vectorially to give the total resultant $\boldsymbol{J}$. That is,

$$[(\boldsymbol{s}_1\boldsymbol{l}_1), (\boldsymbol{s}_2\boldsymbol{l}_2), \ldots] = (\boldsymbol{j}_1, \boldsymbol{j}_2, \ldots) = \boldsymbol{J}$$

Of the above two schemes of coupling, (i) is known by spectroscopists to occur most often in spectra. It was first recognised by Russell and Saunders and is consequently known after them. $\boldsymbol{S}$ in this scheme is the resultant spin moment and $\boldsymbol{L}$ the resultant orbital moment.

The (ii) type of coupling is known as (jj) coupling and is known to occur in certain cases.

For atoms which have a single valency electron, the alkali atoms for example, s was given a value $1/2$. For a similar atom with two valency electrons the resultant S will have a value either $(1/2+1/2)=1$ or $(1/2-1/2)=0$. Similarly for three electrons $S=1/2$ or $3/2$, for four $S=0$, 1 or 2, etc. In general, for x electrons S can take all values up to $x/2$, differing by unity. That is, for x even $S=0, 1, 2 \ldots x/2$, and for x odd $S=1/2, 3/2, 5/2 \ldots x/2$.

The resultant orbital moment L is obtained from the individual l moments in a more involved manner. For two electrons L traverses the values

$$|\, l_1 - l_2 \,| \leq L \leq l_1 + l_2$$

For more than two electrons the possible values for L are obtained by first combining two l's and then combining each possible resultant with the third l, etc. The value for L is always integral.

The resultant moments S and L further combine to give the total angular momentum J. For given values of L and S, the J values are limited by

$$|L-S| \leq J \leq L+S$$

When an atom contains an odd number of electrons J is a half integer. With an even number of electrons it is an integer.

12. TERM MULTIPLICITIES

In an atom having, say, two valency electrons, each characterised by $\boldsymbol{s}_1\boldsymbol{l}_1$ and $\boldsymbol{s}_2\boldsymbol{l}_2$ vectors, the spin vectors $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$ are each equal to 1/2 and the associated quantum number S can assume the values 0 or 1. The resultant orbital moment L is obtained as before:

$$|l_1-l_2| \leq L \leq l_1+l_2$$

For the case $S=1$, J can take three values for each L value, giving

$$J=L-1, \quad L, \quad L+1$$

The J term, therefore, is a threefold term and will give rise to characteristic triplet lines in the spectrum.

For $L=0$ the above reduces to

$$J=S=1$$

It is customary to call this state also a 'triplet state' or 'triplet term', since S here has the value 1.

When $S=0$ all the states are single and are called 'singlets'.

In general, the value of S determines the 'multiplicity' of the spectral terms. For given S and L values, J can take $(2S+1)$ possible values provided $L \geq S$. These levels lie closely in a group called a 'multiplet'. The S multiplicities can be given as

$S=0$, singlet	$S=3/2$, quadruplet
$S=1/2$, doublet	$S=2$, quintet
$S=1$, triplet	etc.

To take a particular example, if an atom has one electron in a p orbit ($l_1=1$) and another in a d orbit ($l_2=2$), then the resultant L can take the values 1, 2, 3. With each value of L, J can have the following sets of values:

$S=1$, $L=1$, $J=0, 1, 2$
$L=2$, $J=1, 2, 3$
$L=3$, $J=2, 3, 4$

$S=0$, $L=1$, $J=1$
$L=2$, $J=2$
$L=3$, $J=3$

For the sake of ready reference Table I gives the resultant *J* values, obtained by giving *L* values from 0 to 4 and *S* from 0 to 7/2.

TABLE I

J VALUES FOR MULTIPLETS

State	Values of *J*	Values of *J*
	Singlets $S=0$	Doublets $S=1/2$
L = 0 *S*	0	1/2
1 *P*	1	1/2 3/2
2 *D*	2	3/2 5/2
3 *F*	3	5/2 7/2
	Triplets $S=1$	Quartets $S=3/2$
L = 0 *S*	1	3/2
1 *P*	0 1 2	1/2 3/2 5/2
2 *D*	1 2 3	1/2 3/2 5/2 7/2
3 *F*	2 3 4	3/2 5/2 7/2 9/2
	Quintets $S=2$	Sextets $S=5/2$
L = 0 *S*	2	5/2
1 *P*	1 2 3	3/2 5/2 7/2
2 *D*	0 1 2 3 4	1/2 3/2 5/2 7/2 9/2
3 *F*	1 2 3 4 5	1/2 3/2 5/2 7/2 9/2 11/2
	Septets $S=3$	Octets $S=7/2$
L = 0 *S*	3	7/2
1 *P*	2 3 4	5/2 7/2 9/2
2 *D*	1 2 3 4 5	3/2 5/2 7/2 9/2 11/2
3 *F*	0 1 2 3 4 5 6	1/2 3/2 5/2 7/2 9/2 11/2 13/2

It may be noted that when the number of valency electrons in an atom is even, the resultant spin vector *S* has integral values; and the above table shows that the number of spectral terms is odd. With odd numbers of valency electrons, *S* has half integral values and the term multiplicities are even.

13. TERM SYMBOLS

The energy states of an atom as defined by *L* and *S* states are conveniently expressed in the form of symbols: *

L	=0	1	2	3	4	5	6	7	8	9	10	11	12	etc.
Symbol	*S*	*P*	*D*	*F*	*G*	*H*	*I*	*K*	*L*	*M*	*N*	*O*	*Q*	etc.

It is customary also to add to the atomic term symbol for *L* a superscript to the left side to give the multiplicity of the term $(2S+1)$.

---

* The *L* of the *S*, *P*, *D*, *F* symbols should not be confused with the *L* denoting the resultant orbital moment, though both of them are written similarly.

Further, the corresponding J value 1, 2 or 3, etc., is added as a subscript on the right side of the term symbol for L. For instance, in the example discussed above, the symbolic notation can be given as:

$$\begin{array}{llllllll} S=1, & L=1, & {}^3P_0, & {}^3P_1, & {}^3P_2 & \text{for} & J=0, & 1, \quad 2 \\ & L=2, & {}^3D_1, & {}^3D_2, & {}^3D_3 & \text{for} & J=1, & 2, \quad 3 \\ & L=3, & {}^3F_2, & {}^3F_3, & {}^3F_4 & \text{for} & J=2, & 3, \quad 4 \end{array}$$

To illustrate by another example:

${}^6P$ means: $(2S+1)=6$, or $S=5/2$, and P stands for the orbital momentum $L=1$. Consequently the possible values for J are 3/2, 5/2, 7/2, which can be separately written as ${}^6P_{3/2}$, ${}^6P_{5/2}$, ${}^6P_{7/2}$. Although the theoretical term multiplicity is sextet, only three J values are actually possible since $L<S$.

14. Multiplet Spectra

The transitions from one multiplet state to another result in the emission of a line complex called a multiplet. The possible number of component spectral lines (or simply 'components') in a multiplet is determined by the selection rule for J (Section 10) which states that only those transitions are allowed for which $\Delta J=0$ or ± 1.

We may illustrate a normal multiplet spectra by considering a transition ${}^5P-{}^5D$ in the neutral Cr atom.

${}^5P$ term means: $S=2, L=1$, possible J values $=1, 2, 3$

${}^5D$ term means: $S=2, L=2$, possible J values $=0, 1, 2, 3, 4$

The transitions can be illustrated by the help of an energy diagram in which the term multiplicities are marked by drawing horizontal lines and the 'allowed' transitions between various multiple bonds are shown by vertical lines. The multiplicity is here seen to be 9 and corresponding to these there will be 9 lines in the spectrum.

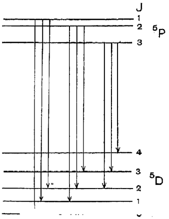

FIG. 28.—Transitions in normal multiplet Cr atom (${}^5P-{}^5D$).

TABLE II

$^5P\ ^5D$ MULTIPLET OF Cr NEUTRAL

	$^5D_4$	$^5D_3$	$^5D_2$	$^5D_1$	$^5D_0$
$^5P_1$	..	..	$^5P_1-{}^5D_2$	$^5P_1-{}^5D_1$	$^5P_1-{}^5D_0$
$^5P_2$	..	$^5P_2-{}^5D_3$	$^5P_2-{}^5D_2$	$^5P_2-{}^5D_1$	..
$^5P_3$	$^5P_3-{}^5D_4$	$^5P_3-{}^5D_3$	$^5P_3-{}^5D_2$	..	..

15. ATOMIC MAGNETIC MOMENT: BOHR MAGNETON

Consider the simplest atom, the hydrogen atom, with an electron revolving in an orbit of radius a_0, with angular velocity ω. The moving electron is equivalent to an electric current, defined as the quantity of electricity traversing a cross-section of the circuit in unit time. Since $\omega/2\pi$ is the number of revolutions which the electron makes per second, the strength of the current is given by $e\omega/2\pi c$ electromagnetic units. The magnetic moment of this circular current (cf. Chapter VI, 1) is given by the product of the current strength and the area of the circuit. Hence the magnetic moment

$$\mu=\frac{e\omega}{2\pi c}\pi a_0^2=\frac{e\omega a_0^2}{2c}$$

As a consequence of the quantum conditions the angular momentum of the circular orbit (also of the more general elliptical orbit) is given by

$$p=\frac{kh}{2\pi}=m_0\omega a_0^2 \quad \text{(from equation 3, Section 1)}$$

Eliminating ωa_0^2, we obtain for the magnetic moment

$$\mu=\frac{e}{2m_0c}p=\frac{eh}{4\pi m_0c}\cdot k \tag{11}$$

which shows that the magnetic moment is equal to $e/2m_0c$ times the orbital moment.

The smallest elementary moment is that obtained by putting $k=1$.

Substituting numerical values in $\frac{eh}{4\pi m_0c}$, the value for elementary moment is given by

$$\mu = 0{\cdot}917 \times 10^{-20} \text{ erg gauss}^{-1}\,*$$

The unit $\frac{h}{2\pi}\,\frac{}{2m_0c}$ is called the 'Bohr magneton', and as the quantum unit of magnetic moment its theoretical significance is the same as that of $\frac{h}{2\pi}$, the quantum unit of mechanical moment.

Referred to a gram-molecule by multiplying the above value by Avogadro's number, the molar Bohr magneton is numerically

$$\mu_B = 5564 \text{ gauss} \times \text{cm. per mole}$$

16. THE LANDE g-FACTOR

The resultant magnetic moment of an atom can be considered to be made up of two vector components:

(i) The component along J of the magnetic moment of the orbital motion, i.e. of $L\left(\frac{h}{2\pi}\right)\left(\frac{e}{2m_0c}\right)$.

(ii) The component along J of the magnetic moment of the spinning electron, i.e. of $2S\left(\frac{h}{2\pi}\right)\left(\frac{e}{2m_0c}\right)$ (cf. Section 5).

The magnitude of the magnetic moment can be calculated by the graphical method of the addition of vectors, as discussed before in Section 7.

As shown in the figure, the component of L along J is $L \cos (\boldsymbol{LJ})$, and that of S along J is $S \cos (\boldsymbol{SJ})$, also $L \cos (\boldsymbol{LJ}) = \frac{J^2+L^2-S^2}{2J}$ and $S \cos (\boldsymbol{SJ}) = \frac{J^2+S^2-L^2}{2J}$.

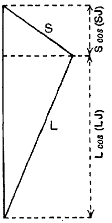

FIG. 29.

Hence the magnetic moment of the atom can be expressed as

$$J \cdot \frac{h}{2\pi} \cdot g \cdot \frac{e}{2m_0c} = [L \cos (\boldsymbol{LJ}) + 2S \cos (\boldsymbol{SJ})] \frac{h}{2\pi}\,\frac{e}{2m_0c}$$

$$= J\frac{h}{2\pi}\left(1 + \frac{J^2+S^2-L^2}{2J^2}\right) \cdot \frac{e}{2m_0c}$$

---

* The numerical values are the most recent and embody Birge's estimate of the most probable values of the atomic constants (cf. Van Vleck, *Electric and Magnetic Susceptibilities*, p. 68).

which gives for the factor g the value within the brackets on the right-hand side. Calculations on the basis of the new quantum mechanics have replaced the magnitudes of J^2, S^2 and L^2 by $J\,(J+1)$, $S\,(S+1)$ and $L\,(L+1)$ respectively. Consequently, we get

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Here g is called the Lande g-factor or Lande splitting factor, and is by definition the ratio of the magnetic to the mechanical moment of an atom—the moments being expressed in their respective quantum units $\frac{h}{2\pi}\cdot\frac{e}{2m_0c}$ and $\frac{h}{2\pi}$.

By way of illustration, we may derive the g-factor for the alkali spectra whose normal state is given by the symbol $^2S_{1/2}$. This gives $(2S+1)=2$ or $S=1/2$, the orbital moment $L=0$ (for term symbol S) and so $J=1/2$, hence $g=2$.

17. THE ZEEMAN EFFECT

Zeeman discovered that the spectral lines in general are split into a number of closely lying components when the emitting light source is placed in a strong magnetic field. In some simple atoms the splitting is quantitatively explained on an early classical theory given by Lorentz. The phenomenon is then called the 'normal Zeeman effect'. The term 'anomalous Zeeman effect' is applied to the more complicated splitting where the Lorentz formula fails completely. In general, the so-called 'anomalous' effect is the one commonly observed.

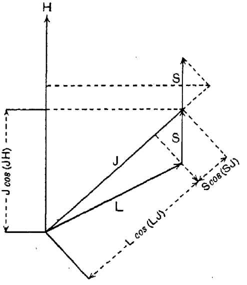

FIG. 30.—Angular momentum vector J of an atom in a magnetic field.

According to Larmor's theorem, a system of moving particles, all having the same ratio of charge to mass, when subjected to an impressed magnetic field, precesses about the direction of the field with a constant angular velocity (cf. Chapter VI, Section 1). We will apply this theorem to our atomic model. Suppose that the coupling between the orbital and spin moments L and S of the atom is so strong that it is not appreciably disturbed by the external magnetic field. The resultant angular moment J will, according to Larmor's theorem precess about the direction of H. The precessional energy will be given by the product of the Larmor velocity of precession o and the projected component of the mechanical moment $J.\frac{h}{2\pi}$ on the direction of H; whence, according to the figure

$$\Delta W_m = o \times J.\frac{h}{2\pi}\cos(\boldsymbol{JH})$$

The projection of $\boldsymbol{J}$ on $\boldsymbol{H}$ is denoted by the quantum vector $\boldsymbol{M}$, corresponding to the magnetic quantum number M. M can have values $+J$ to $-J$ (cf. Section 5), and since J can only change by ± 1, there are in all $(2J+1)$ possible values, and corresponding to these there are $(2J+1)$ possible angles between J and H; which means that in the presence of a magnetic field an atom can only assume certain discrete orientations with respect to the field. The same argument holds even in a vanishingly small field, and the atom is said to be 'spatially quantised'.

Expressed in terms of the magnetic quantum number M, the energy of the precession becomes

$$\Delta W_m = M\frac{h}{2\pi}.g.\frac{eH}{2m_0c} = Mg\frac{eh}{4\pi m_0c}H \quad . \quad . \quad (12)$$

since $o = g\frac{eH}{2m_0c}$* on Larmor's theorem.

The above equation gives the energy difference by which the lines will show Zeeman splitting in a magnetic field of H gauss.

In accordance with deductions of the quantum mechanics the magnetic quantum number M can only change by 0, or ± 1. When $\Delta M = 0$, the emitted line is linearly polarised; with $\Delta M = +1$ or -1, the emitted lines are circularly polarised in opposite senses.

A modification of Zeeman effect known as Paschen-Back effect may be briefly considered. It was assumed in our treatment of the Zeeman effect that the coupling between the orbital and spin moments, L and S of the atom was so strong that it was not appreciably disturbed by the field. When the field becomes very strong the L-S coupling breaks down and the orbital moment L and the spin moment S orient themselves, independently of each other, with respect to the external field. If the vectors $\boldsymbol{M}_{\mathrm{L}}$ and $\boldsymbol{M}_{\mathrm{S}}$ represent the projection of the orbital and spin moments in the field direction and M_{L} and M_{S} the corresponding quantum numbers (cf. Section 6), then the change in the magnetic energy of the atom is given by

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* The Lande g-factor has been introduced here to account for the spin moment of the electron. This factor does not occur in the classical Larmor theorem.

$$\begin{aligned}\Delta W_m &= M_{\mathrm{L}} \cdot \frac{h}{2\pi} \cdot \frac{e}{2m_0c} H + 2M_{\mathrm{S}} \frac{h}{2\pi} \cdot \frac{e}{2m_0c} H \\ &= (M_{\mathrm{L}} + 2M_{\mathrm{S}}) \frac{eh}{4\pi m_0 c} \cdot H \quad . \quad . \quad . \quad (13)\end{aligned}$$

By analogy $(M_{\mathrm{L}} + 2M_{\mathrm{S}})$ may be designated as strong field magnetic quantum numbers.

18. SPECTROSCOPY AND MAGNESCOPY

The importance of Zeeman effect to magnetism lies in the link which it provides between spectroscopic and magnetic properties, and in the optical evidence it affords of the interaction between atoms and an external magnetic field. The equation for Zeeman splitting

$$\Delta W_m = Mg \frac{eh}{4\pi m_0 c} H$$

can be written as

$$\Delta W_m = \mu H \quad . \quad . \quad . \quad . \quad (14)$$

where $\mu = Mg \frac{eh}{4\pi m_0 c}$ is the resolved moment of the atom. Since $\frac{eh}{4\pi m_0 c}$ is the Bohr unit of magnetic moment, the values of Mg give the possible resolved magnetic moments of the atom in terms of the Bohr magnetons. The values of μ obtained from purely magnetic measurements and their bearing on theory will be discussed in subsequent chapters.

19. STERN AND GERLACH EXPERIMENT

An experiment of great interest was suggested by Stern in 1921. It sought to test the number of discrete orientations of spatially quantised atoms in an external magnetic field.

The expression $Mg \frac{eh}{4\pi m_0 c}$, discussed above, gives the values of the possible resolved magnetic moments along the direction of the applied field. The magnetic quantum number M can assume the $(2J+1)$ values 0, ± 1, ± 2 . . . $\pm J$ if J is an integer or $\pm 1/2$, $\pm 3/2$ . . . $\pm J$ if J is half integer. If a stream of such atoms is directed through a non-homogeneous field, the magnetic elements will be acted upon by a force.

$$Mg\frac{eh}{4\pi m_0 c}\frac{\delta H}{\delta s}$$

where $\frac{\delta H}{\delta s}$ is the gradient of the magnetic field. The atoms characterised by different values of J will, in consequence, deviate from the original direction by the factor Mg. For atoms in the normal $^2S_{1/2}$ state, for example, since $J=\pm 1/2$, M can only assume the values $+1/2$ and $-1/2$, g for this state is 2 and Mg will have the possible values $+1$ and -1. Two patterns corresponding to these values were found by Stern and Gerlach for silver atoms. Similar Stern-Gerlach patterns were found for hydrogen, copper, gold, sodium and potassium atoms also, in conformity with the spectroscopic assignment of the same $^2S_{1/2}$ ground state to them. For atoms which have $J=0$, like Zn and Cd ($^3P_0$) or Pb and Sn ($^1S_0$), the values for g and Mg are both zero and experimentally no splitting of the atomic beam is observed. The bismuth atom is an interesting exception and is explained on the ground that the L-S coupling in this atom is not of the Russell-Saunders type.

For convenience of reference Tables of g and Mg values for a few of the spectroscopic states are given below.

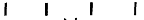
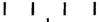
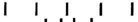
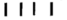
TABLE III

THE LANDE SPLITTING FACTOR g. (RUSSELL-SAUNDERS COUPLING)

L \ J		0	1	2	3	4	5	1/2	3/2	5/2	7/2	9/2	11/2		J / L
						Singlets	$S=0$					Doublets	$S={}_{1/2}$		
0	^1S	0/0						2						^2S	0
1	^1P		1					2/3	4/3					^2P	1
2	^1D			1					4/5	6/5				^2D	2
3	^1F				1					6/7	8/7			^2F	3
4	^1G					1					8/9	10/9		^2G	4
						Triplets	$S=1$					Quartets	$S={}_{3/2}$		
0	^3S		2						2					^4S	0
1	^3P	0/0	3/2	3/2				8/3	26/15	8/5				^4P	1
2	^3D		1/2	7/6	4/3			0	6/5	48/35	10/7			^4D	2
3	^3F			2/3	13/12	5/4			2/5	36/35	78/63	4/3		^4F	3
4	^3G				3/4	21/20	6/5			4/7	62/63	116/99	14/11	^4G	4

TABLE IV

Mg VALUES AND STERN-GERLACH PATTERNS

Normal State	*g*	*Mg*	Atomic Ray Pattern
$^1S_0$	0/0	0	
$^2S_{1/2}$	2	−1 +1	
$^4S_{3/2}$	2	−3 −1 +1 +3	
$^2P_{1/2}$	2/3	−1/3 +1/3	
$^2P_{3/2}$	4/3	−6/3 −2/3 +2/3 +6/3	
$^3P_0$	0/0	0	
$^3P_2$	3/2	−6/2 −3/2 0 +3/2 +6/2	
$^2D_{3/2}$	4/5	−6/5 −2/5 +2/5 +6/5	

20. X-RAY SPECTRA AND INNER LEVELS

The optical spectra arise from transitions of the outermost valency electrons of the atom while the inner electrons remain more or less unaffected. It is possible, however, to remove one of the electrons from an inner shell of the atom by suitable means of excitation. Since the inner electrons are more firmly bound to the atomic nucleus, they require a larger amount of energy to remove them. This may be obtained by bombardment of the atom with electrons of very high velocity or by absorption of energy of much higher frequency than that of light. The vacancy caused by the removal of the inner electron can be filled by an electron from one of the outer shells of the atom. The outer shell in its turn can get an electron from another shell farther out, and so on till finally the atom-ion captures a free electron and returns to its original state. Each electronic jump in the inner shells of the atom is accompanied by the emission of a characteristic monochromatic radiation of X-rays. As the energy changes in the inner transitions are very large the emitted spectral lines have very short wavelengths. X-rays are roughly classed as 'hard' and 'soft', the harder rays having the shorter wavelengths, about 0·01 A° to 1 A°, and the softer from 1 A° to 10 A°. According to X-ray spectroscopy the inner levels of the atom are denoted by the letters *K*, *L*, *M*, *N*, *O*, *P*, etc., the *K* shell being the innermost.

21. THE SCREENING CONSTANT

The vector atomic model rests on the assumption that there is a central field of force due to the nucleus. In an atom containing several electrons distributed over various shells, the inner electrons form a sort of 'screen' over the force field of the positive nucleus. It is usual to give the name 'kernel' or 'atom core' to the stable electron group obtained after removing the valency electrons. In the alkali atom potassium, for example, removing the valence electron will leave the atom with the configuration of the nearest inert gas argon. The ions Mg^{++}, Al^{+++}, Tl^{++++} will have the neon configuration. Since the kernel contains electronic shells with elliptical or circular orbits it may be considered to resemble a spherical volume charge with the density of charge varying from centre outwards. For simplicity, however, we may regard the atom core as a positive nucleus surrounded by a uniformly charged spherical surface, so that the net attracting charge is $(Z-s)e$ outside the spherical surface and Ze inside the surface, where Z is the atomic number and s is called the screening constant.

22. Penetrating and non-penetrating Orbits

For a certain distribution of spherical surface charge the orbit of the valency electron may be one of two kinds: (*a*) non-penetrating and (*b*) penetrating, as represented in Figs. 31A and 31B.

When the orbit is large it may lie entirely outside of the spherical charge surface and resemble closely a hydrogen-like orbit in an atom with nuclear charge Ze. This is the non-penetrating orbit and is distinguished by its small interaction with the atom core from the type of orbit which penetrates the charge surface and in consequence moves in a different field force for part of the revolution. As a result of the penetration the outer elliptical orbit undergoes a precession about an axis normal to its plane, and the electron, therefore, penetrates the charge surface at a different point, the same distance apart, in each successive revolution.

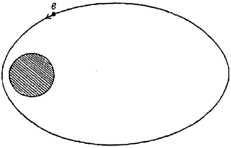


FIG. 31A.—A non-penetrating orbit. The shaded circle represents the atom core.

The valence electron in alkali-like atoms is known to have a penetrating orbit. The sodium atom, for instance, consists of a nuclear charge of Ze $(Z=11)$. This is surrounded by a very small charge sphere of $-2e$ due to the two 1*s* electrons in the *K* shell, and a larger shell of charge $-8e$ due to two 2*s* and six 2*p* electrons. The inner electron charge may be regarded as coincident with the nuclear charge. Hence, outside of the charge sphere the effective charge attracting the valence electrons is $Z_e e$, where

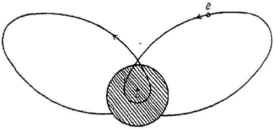


FIG. 31B.—A penetrating orbit. The shaded circle represents the atom core which the electron penetrates in its orbital path.

$$Z_e e = (Z - 10)e = e$$

and inside the charge sphere it is

$$Z_i e = (Z - 2)e = 9e$$

The 3*p* electron in sodium, therefore, moves in a field of effective nuclear charge varying from *e* to about 9*e* as it traverses the inner part of its orbit.

For a 3*p* electron in the non-penetrating mercury orbit the variation of effective nuclear charge is between the narrow limits of about 70*e* and 78*e*.

23. THE ARRANGEMENT OF ELECTRONS IN ATOMS—PAULI'S EXCLUSION PRINCIPLE

A principle of fundamental importance to many branches of spectroscopy is the 'exclusion principle' enunciated by Pauli. It may be expressed as follows:

An atom cannot exist in a quantum state such that two or more of the electrons within it have the values of all of their four quantum numbers identical in the presence of a strong magnetic field; in other words, no two electrons in an atom can have an identical set of quantum numbers in a magnetic field.

In assigning electrons to the various groups and sub-groups in the atom, two conditions have to be satisfied: (i) the electron configuration must be permitted by the Pauli's principle and (ii) it should be such that the energy of the atom is a minimum.

The four quantum numbers considered by the Pauli principle are:

$$n = 1, 2, 3 \ldots \infty$$
$$l = 0, 1, \ldots, n-1$$
$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l$$
$$m_s = \pm 1/2$$

For the total quantum number $n=1$, l can only take the value 0 and therefore m_l must also be 0 and $m_s = \pm 1/2$. Thus, for $n=1$, $l=0$ there can only be two electrons in the atom, one with $m_s = +1/2$ and the other with $m_s = -1/2$. These two electrons complete the innermost or K shell of the atom. For $n=2$, l can take the values 0 or 1; when $l=0$, $m_l=0$ and m_s may be $= \pm 1/2$, so two electrons may occupy the (2,0) sub-shell; with $l=1$, m_l may take the three values, -1, 0, $+1$ and corresponding to each of these m_s has the two values $\pm 1/2$, so that in all six electrons may occupy the (2, 1) sub-shell. This gives a total of eight electrons to the L shell of the atom.

In general m_l has a total of $(2l+1)$ values, for each of which m_s can be either $+1/2$ or $-1/2$, and the total number of electrons in nth shell is

$$\sum_{l=0}^{l=(n-1)} 2(2l+1) = 2n^2$$

Thus $2n^2$ is the number of electrons with the total quantum number n which are allowed in an atom by the Pauli principle. These $2n^2$ electrons form a completed shell or group. The distribution of electrons in the successive shells and sub-shells is shown in the following table.

TABLE V

X-Ray Shell	n, l	Sub-groups $2(2l+1)$	Completed Groups $2n^2$
K	1, 0	2	2
L	2, 0	2	
	2, 1	6	8
M	3, 0	2	
	3, 1	6	
	3, 2	10	18
N	4, 0	2	
	4, 1	6	
	4, 2	10	
	4, 3	14	32
O	5, 0	2	
	5, 1	6	
	5, 2	10	
	5, 3	14	
	5, 4	18	50 etc.

The K shell (with $n=1$) is completed with the inert gas helium. Further addition of electrons in the succeeding elements takes place in the L shell, which can take its quota of eight electrons, thus making up a total of ten electrons in the K and L completed groups. The element with atomic number $Z=10$ is the rare gas neon. Additional electrons now begin to occupy the M shell. It is noteworthy that as each succeeding electron is added the properties of the elements show striking similarities with the corresponding elements of the L shell. Thus, lithium with one electron in the L shell is similar to sodium with one electron in the M shell, beryllium is similar to magnesium and so on.

The process of atom-building as successive electrons are added is given in Table VI.* The last column of the table gives the term notation for the normal stable state of the atom.

The inert gases occupy an interesting position in the table. The first inert gas helium completes the K shell. Neon has the configuration $1s^2 2s^2 2p^6$ and completes the L shell. Argon has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6$ and completes the s and p sub-groups of the M shell. Similarly, krypton, xenon and radon complete the s^2 and p^6 sub-groups of N, O and P shells, respectively. The completed s^2 and p^6 sub-groups are marked by their strong binding energy, and the chemically 'inert' nature of these gases is clearly explained on this basis. Thus, the ionisation potential of hydrogen is 13·54 volts, that of He is 24·48 volts, for the next element Li it falls to 5·37 volts. Fluorine (9) has the ionisation potential of 16·9 volts, Ne (10) has 21·5 volts, and for the alkali Na (11) it falls again to 5·12 volts.

It will be seen from the table that the first eighteen electrons are bound in the order of increasing n and l and the sub-shells contain the maximum number of electrons required on the Pauli exclusion principle. At potassium (19) the first irregularity is encountered in this respect. The quantum theory permits ten electrons to occupy the 3, 2 sub-shell. With argon the 3, 1 sub-shell is just completed and at potassium we should expect an electron to occupy the 3, 2 sub-shell. It is known, however, from the spectrum of potassium that its outer electron occupies the 4, 0 sub-shell. The spectroscopic normal level for potassium is ${}^2S_{1/2}$, with the outer configuration $3s^2 3p^6 4s$, and this has lesser energy

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* The original form of the table is due to Bohr, but the assignment of the electrons in the sub-levels is essentially due to Stoner and Main-Smith.

TABLE VI

Element		K	L		M			N		Normal term (theoretical)
		1, 0 1s	2, 0 2s	2, 1 2p	3, 0 3s	3, 1 3p	3, 2 3d	4, 0 4s	4, 1 4p	
H	1	1	..	..	..	..	..	..	..	$^2S_{1/2}$
He	2	2	..	..	..	..	..	..	..	$^1S_0$
Li	3	2	1	..	..	..	..	..	..	$^2S_{1/2}$
Be	4	2	2	..	..	..	..	..	..	$^1S_0$
B	5	2	2	1	..	..	..	..	..	$^2P_{1/2}$
C	6	2	2	2	..	..	..	..	..	$^3P_0$
N	7	2	2	3	..	..	..	..	..	$^4S_{3/2}$
O	8	2	2	4	..	..	..	..	..	$^3P_2$
F	9	2	2	5	..	..	..	..	..	$^2P_{3/2}$
Ne	10	2	2	6	..	..	..	..	..	$^1S_0$
Na	11	10 Neon configuration $1s^22s^22p^6$			1	..	..	..	..	$^2S_{1/2}$
Mg	12				2	..	..	..	..	$^1S_0$
Al	13				2	1	..	..	..	$^2P_{1/2}$
Si	14				2	2	..	..	..	$^3P_0$
P	15				2	3	..	..	..	$^4S_{3/2}$
S	16				2	4	..	..	..	$^3P_2$
Cl	17				2	5	..	..	..	$^2P_{3/2}$
A	18				2	6	..	..	..	$^1S_0$
K	19	18 Argon configuration $1s^22s^22p^63s^23p^6$					..	1	..	$^2S_{1/2}$
Ca	20						..	2	..	$^1S_0$
Sc	21						1	2	..	$^2D_{3/2}$
Ti	22						2	2	..	$^3F_2$
V	23						3	2	..	$^4F_{3/2}$
Cr	24						5	1	..	$^7S_3$
Mn	25						5	2	..	$^6S_{5/2}$
Fe	26						6	2	..	$^5D_4$
Co	27						7	2	..	$^4F_{9/2}$
Ni	28						8	2	..	$^3F_4$
Cu	29	28 Copper core $1s^22s^22p^63s^23p^63d^{10}$						1	..	$^2S_{1/2}$
Zn	30							2	..	$^1S_0$
Ga	31							2	1	$^2P_{1/2}$
Ge	32							2	2	$^3P_0$
As	33							2	3	$^4S_{3/2}$
Se	34							2	4	$^3P_2$
Br	35							2	5	$^2P_{3/2}$
Kr	36							2	6	$^1S_0$

TABLE VI—(*continued*)

Element	Configuration of Inner Shells	*N*		*O*			*P*	Normal Term (theoretical)
		4, 2 4*d*	4, 3 4*f*	5, 0 5*s*	5, 1 5*p*	5, 2 5*d*	6, 0 6*s*	
Rb 37	36 Krypton configuration $1s^2 2s^2 2p^6 3s^2 3p^6$ $3d^{10} 4s^2 4p^6$	..	..	1	..	..	..	$^2S_{1/2}$
Sr 38		..	..	2	..	..	..	$^1S_0$
Y 39		1	..	2	..	..	..	$^2D_{3/2}$
Zr 40		2	..	2	..	..	..	$^3F_2$
Cb 41		4	..	1	..	..	..	$^6D_{1/2}$
Mo 42		5	..	1	..	..	..	$^7S_3$
Ma 43		6	..	1	..	..	..	$^6D_{9/2}$
Ru 44		7	..	1	..	..	..	$^5F_5$
Rh 45		8	..	1	..	..	..	$^4F_{9/2}$
Pd 46		10	..	..	..	..	..	$^1S_0$
Ag 47	46 Palladium configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 4d^{10}$		..	1	..	..	..	$^2S_{1/2}$
Cd 48			..	2	..	..	..	$^1S_0$
In 49			..	2	1	..	..	$^2P_{1/2}$
Sn 50			..	2	2	..	..	$^3P_0$
Sb 51			..	2	3	..	..	$^4S_{3/2}$
Te 52			..	2	4	..	..	$^3P_2$
I 53			..	2	5	..	..	$^2P_{3/2}$
Xe 54			..	2	6	..	..	$^1S_0$
Cs 55	54 Xenon configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 4d^{10} 5s^2 5p^6$ The shells 1*s* to 4*d* contain 46 electrons		..			..	1	$^2S_{1/2}$
Ba 56			..			..	2	$^1S_0$
La 57			..			1	2	$^2D_{3/2}$
Ce 58			1			1	2	$^3H_4$
Pr 59			2	The shells 5*s* and 5*p* contain 8 electrons $5s^2 5p^6$		1	2	$^4K_{11/2}$
Nd 60			3			1	2	$^5L_6$
Il 61			4			1	2	$^6L_{11/2}$
Sm 62			5			1	2	$^7K_4$
Eu 63			6			1	2	$^8H_{3/2}$
Gd 64			7			1	2	$^9D_2$
Tb 65			8			1	2	$^8H_{17/2}$
Dy 66			9			1	2	$^7K_{10}$
Ho 67			10			1	2	$^6L_{21/2}$
Er 68			11			1	2	$^5L_{10}$
Tu 69			12			1	2	$^4K_{17/2}$
Yb 70			13			1	2	$^3H_6$
Lu 71			14			1	2	$^2D_{3/2}$

TABLE VI—(*continued*)

Element	Configuration of Inner Shells	*O*		*P*			*Q*	Normal Term (theoretical)
		5, 2 5*d*	5, 3 5*f*	6, 0 6*s*	6, 1 6*p*	6, 2 6*d*	7, 0 7*s*	
Hf 72		2	..	2	..	..	..	$^3F_2$
Ta 73		3	..	2	..	..	..	$^4F_{3/2}$
W 74		4	..	2	..	..	..	$^5D_0$
Re 75		5	..	2	..	..	..	$^6S_{5/2}$
	68	6	..	1	..	..	..	$^6D_{9/2}$
Os 76	Hafnium core	6	..	2	..	..	..	$^5D_4$
	1*s* to 5*p*	7	..	1	..	..	..	$^5F_5$
Ir 77		7	..	2	..	..	..	$^2D_{5/2}$
		8	..	1	..	..	..	$^4F_{9/2}$
Pt 78		9	..	1	..	..	..	$^3D_3$
		10						
Au 79			..	1	..	..	..	$^2S_{1/2}$
Hg 80			..	2	..	..	..	$^1S_0$
Tl 81			..	2	1	..	..	$^2P_{1/2}$
Pb 82	78		..	2	2	..	..	$^3P_0$
Bi 83	Gold core		..	2	3	..	..	$^4S_{3/2}$
Po 84	1*s* to 5*d*		..	2	4	..	..	$^3P_2$
85			..	2	5	..	..	$^2P_{3/2}$
Rn 86			..	2	6	..	..	$^1S_0$
87	86		..			..	1	$^2S_{1/2}$
Ra 88	Radon configuration		..			..	2	$^1S_0$
Ac 89			..			1	2	$^2D_{3/2}$
Th 90			1	The shells		1	2	$^3H_4$
	The shells 1*s* to		..	6*s* and 6*p*		2	2	$^3F_2$
Pa 91	5*d* contain 78		2	contain 8		1	2	$^4K_{11/2}$
	electrons		..	electrons		3	2	$^4F_{3/2}$
Ur 92			3			1	2	$^5D_6$
			..			4	2	$^5D_0$

than the levels $^2D_{3/2,\ 5/2}$, corresponding to the configuration $3s^2 3p^6 3d$. Ionised calcium has a structure similar to K, and the two electrons of Ca are in the 4*s* state. The elements Sc (21) to Ni (28) are interesting, as they have electrons in both 3, 2 and 4, 1 sub-groups. The variable valency and well-known magnetic properties of these elements are, no doubt, due to these partially occupied groups. Copper (29) has a completed *M* shell as the sub-group 3, 2 is completely filled up with ten electrons, and there is, in addition, one 4*s* electron. Copper has $^2S_{1/2}$ state similar to the alkalis Li, Na, K. But unlike the alkalis, the underlying sub-shell in Cu is 3, 2, while in the alkalis it is the inert gas core. The 3, 2 sub-shell can lose one electron fairly easily, and consequently copper can be divalent at times, but the underlying sub-shell $3p$ in potassium has a much higher binding energy. Other differences in the chemical properties of K and Cu can be accounted for, to some extent at least, on the difference in the size of the atomic core, as due to the higher nuclear charge $(Z-e)$ will be much smaller in Cu than in K.

With krypton (36) the M level and the sub-groups $4s$ and $4p$ are all completed. The added electron in Rb (37) does not go into the N shell, but like potassium goes into the next shell O. At Yttrium (39), an electron occupies $4d$ orbit which is then filled up with ten electrons at Pd (46). Ag (47) has the configuration $4s^2 4p^6 4d^{10} 5s$, with one electron in the 5, 0 sub-shell. From Ag (47) to Xe (54), the sub-groups 5, 0 and 5, 1 are regularly filled up, the inner 4, 3 sub-group being still unoccupied.

Cs (55) with a $6s$ electron is similar to the alkalis K and Rb. Ba (56), similarly to Ca and Sr, has two $6s$ electrons. With La (57) one electron enters the inner 5, 2 sub-group, and while the $4f$ sub-group is being filled up from Ce (58) to Lu (71), the 5, 2 and 6, 0 sub-groups remain unchanged. The properties of the rare earth metals differ remarkably from the rest of the elements inasmuch as there is no $4f$ analogue in any of the earlier periods. The rare earths thus form a segregated group of their own, with allied chemical properties because of the similar outer valence electrons.

In the elements Hf (72) to Au (79) the sub-groups 5, 2 and 6, 0 are occupied similarly to the transitional elements Rb (37) to Ag (47), and the chemical properties of the two are similar in many respects. Au (79) to Rn (86) the sub-shells 6, 0 and 6, 1 are regularly filled up. Au has one s electron outside of a shell of eighteen and is thus similar to Ag and Cu. In the subsequent elements, the unknown alkali 87 to Ur (92) the 7, 0 sub-group is occupied and partially the $6d$ and $5f$ sub-shells.

24. MOLECULAR STATES

The molecular electronic states are of a similar type to the atomic states in a strong axially symmetrical field. The multiplets observed in the molecular spectra find their prototypes in the multiplets given by the strong field electronic levels. The symbol Λ is used in place of the strong field quantum number $|M_L|$ which for a multiplet has the same meaning as L in an atomic multiplet. The component of the spin quantum number $\pm M_S$ is denoted by Σ and plays the same rôle as S in determining multiplicity. The symbol Ω has the same meaning as J in atomic multiplets. Also

$$\Omega = |\Lambda + \Sigma| = |M|$$

(if $\Lambda = 0$, Σ and Ω do not exist as quantum numbers).

Ω can take the values:

$$\Lambda + S,\ \Lambda + S - 1,\ \ldots,\ |\Lambda - S|$$

and Λ is always $\geqq 0$. Similarly to atomic multiplets the molecular multiplets can be designated by symbols such as ${}^1\Pi$, ${}^2\Sigma$, ${}^3\Pi_2$, ${}^3\Pi_1$, etc. The superscript in these gives the term multiplicity $M (M = 2S + 1)$ exactly as for an atomic state.

The symbols	Σ	Π	Δ	Φ	T	
stand for	$\Lambda = 0$	1	2	3	4	etc.

The subscript on the right gives the value $\Lambda + \Sigma$ rather than Ω. When $\Lambda + \Sigma \geqq 0$, Ω is identical with $\Lambda + \Sigma$. For singlet levels no subscript is necessary since Σ has only one value 0.

The above description of molecular notation is very incomplete owing to the great complexity of molecular spectra.

25. THE VECTOR ATOM MODEL AND QUANTUM MECHANICS

A new orientation to the outlook on spectroscopy and atomic structure has been given in recent years by the pioneer work of Heisenberg, Schrödinger and De Broglie.

The development of the quantum mechanics has taken away much of the physical definiteness of the orbital picture of the atom. It is still customary, however, to base spectroscopic discussion upon a visualisable atomic model—the vector model. At best the model is an approximation, and its justification is only its utility in providing a mental picture which helps in the interpretation and deduction of results, in suggesting new lines of experimental and theoretical approach and in permitting simple derivation of formulas whose rigorous development is beset with mathematical difficulties. The quantum mechanics has served to emphasise the usefulness of the vector model by limiting clearly its sphere of application.

The mathematical background of wave-mechanics has taken the following three forms:

(i) The Matrix theory of Heisenberg, Born and Jordan, and Dirac.

(ii) The wave-mechanics of Schrödinger.

(iii) The 'transformation theory' developed by Dirac, Jordan and interpreted by Heisenberg.

When dealing with particles like atoms or electrons, Schrödinger associates the particles with certain groups of waves; De Broglie imagines that the particle and the wave are associated, so that the particle is guided in its path by the waves. It is clear, however, that whether we give a physical significance to the waves or regard them merely as a certain distribution of probability function, we have to admit the existence of a duality of wave and particle, the wave character being more obvious the lighter the particle.

The quantum mechanical theory has been extremely successful in bringing about a rapprochement between the classical theory of dynamics and the old quantum theory. The characteristic quantum numbers, for example, find a natural derivation on this theory as they turn out to be parameters defining the solutions of the differential equation for the atom model. The azimuthal and principal quantum numbers and the conception of the spin electrons are thus easily accounted for. We are not asked to give up the familiar electronic model of the atom, because whether we regard the electron as a charged particle revolving in an orbit or as a train of waves, the results of the wave mechanical analysis are capable of being interpreted in terms of the pictorial electronic model.

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CHAPTER VI

DIAMAGNETISM

In a classical paper in 1905 Langevin[1] gave a new outlook on the facts of para- and diamagnetism. Soon after the discovery of the fundamental facts of magnetism by Faraday in 1845 Weber[2] made use of Ampère's hypothesis of molecular currents in developing a 'molecular current' theory of magnetism. It remained, however, for the celebrated French physicist to apply the concepts of the electronic hypothesis to formulate an exact mathematical theory which provided a very satisfactory explanation of both para- and diamagnetism. According to the electron theory of matter the atom could be considered to be made up of a positive nuclear charge surrounded by electrons moving in closed orbits. These moving electrons were made to explain the magnetic properties of the atom. Since Langevin's treatment was not based on any specific assumption, it could be modified to accord with the later quantum developments.

1. THEORY OF DIAMAGNETISM

The electrons in an atom are assumed to be moving in closed orbits producing at a distance magnetic effects similar to those arising from a current circuit.

Consider for simplicity an atom in Fig. 32 in which an electron is shown revolving in its orbit in a counter clockwise direction. According to the classical electron theory an electron carrying a negative charge e (e.s.u.) and moving in a circular orbit of radius r_1 is equivalent to a circular current. If ω is the angular velocity of the electron, then $\frac{\omega}{2\pi}$ is the number of revolutions which it will make per second, and the strength of the current, measured as the quantity of electricity that passes through the cross-section per second, is given by

$$\frac{e\omega}{2\pi} \text{ e.s.u.} \quad \text{or} \quad \frac{e}{c} \cdot \frac{\omega}{2\pi} \text{ e.m. units}$$

In the figure, since the electron is shown revolving in a counter clockwise direction, the equivalent current will flow in a clockwise direction. A magnetic field due to the revolving electron will consequently be established in a direction perpendicular to the plane of the electronic orbit and directed as shown by the arrow. The magnetic moment of this circular current is given by the fact that the current strength multiplied by the area of the bounded surface around which the current flows is equal to the moment of the elementary magnet placed at right angles to the current surface. Hence the magnetic moment μ_e is given by

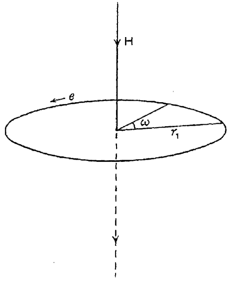


FIG 32.—Orbit of a Revolving Electron.

$$\mu_e = \frac{e\omega}{2\pi c} \cdot \pi r_1^2 = \frac{e\omega r_1^2}{2c} \quad . \quad (1)$$

Also, the moving electron is subject to a centrifugal force which is equal and opposite to the attraction of the nucleus and is given by

$$F = m\omega^2 r_1 \quad . \quad . \quad . \quad . \quad (2)$$

where m is the mass of an electron.

If now a magnetic field H is applied perpendicular to the plane of the orbit, the revolving electron will experience a force, $\frac{He\omega r_1}{c}$ directed along the radius, the sense of which will depend upon the direction of the magnetic field and of the moving electron.

When the magnetic moment μ_e and the field have the same direction the force on the electron is directed away from the nucleus, but when μ_e and H are oppositely directed the force is towards the nucleus. Hence the changed value of the centrifugal force in the presence of the impressed field is given by

$$F - \frac{He\omega r_1}{c}$$

The result of this can be expressed on the basis of a theorem given by Larmor[3]. This theorem describes the behaviour of a system of particles, all having the same ratio of charge to mass, in the presence of a constant uniform magnetic field H. According to Larmor's theorem, 'the superimposed field H leaves the form of the orbits and their inclination to the magnetic lines of force, as also the motion in the orbit, unaltered and merely leads to the addition of a uniform "precession" of the orbit about the direction of the lines of force'. This simply means that the motion of the system is the same as it would be in the absence of the field, except that a uniform rotation around an axis parallel to the field is superposed. The velocity of this rotation is given by $o=-\frac{eH}{2mc}$.

Hence the effect of the field is merely to accelerate or retard the electron in its orbit by an amount

$$o=-\frac{eH}{2mc} \quad . \quad . \quad . \quad . \qquad (3)$$

This causes a variation in the magnetic moment of the electron by an amount $\Delta\mu_e$ given by

$$\Delta\mu_e=\frac{er_1^2}{2c}\{(\omega+o)-\omega\}=\frac{eo}{2c}r_1^2 \quad \text{from (1)}$$

$$\frac{e^2H}{4mc^2}\,\imath^2 \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

in which the negative sign indicates that an increasing magnetic field tends to induce currents which produce a field opposite in direction to the inducing field. Thus the electronic orbits which give a field opposite to H will be accelerated while the electronic orbits giving a field in the same direction will be retarded.

The above equation has been derived for one electron, but it can be easily extended to atoms containing more than one electron. Larmor's theorem which we have made use of in the above derivation is valid for any number of charged particles having the same value for e/m. With more than one electron the summation has to be extended over all of them and r_1^2 is replaced by $\underset{n}{\Sigma r_1^2}$. Also, as all the orbits are not circular, the r_1^2 values should be taken to be average values denoted by $\overline{r_1^2}$. Further, the field was, for simplicity, assumed to be perpendicular to the orbit of the electron, but the orbital planes can have all possible orientations with respect to it, and consequently the radii considered would take the projected values perpendicular to the applied field. Finally, $\overline{r_1^2}$ becomes the mean square of the radius of a projected orbit in a plane perpendicular to the magnetic field and $\underset{n}{\Sigma}\overline{r_1^2}$ the summation extended over all the electrons constituting the atom. Hence

$$\Delta\mu_e = -\frac{e^2\mathrm{H}}{4mc^2}\underset{n}{\overline{\Sigma r_1^2}} \quad . \quad . \quad . \quad (5)$$

Further, we assume that the atom is spherically symmetrical. By this we mean that if the radius r_1 at any instant has the coordinates x_1, y_1, then for a time average $\overline{x_1^2+y_1^2}=\overline{r_1^2}$, which gives

$$\overline{\Sigma r_1^2}=\tfrac{2}{3}\overline{\Sigma r^2}$$

and the diamagnetic atomic moment due to the presence of the field becomes

$$\Delta\mu_e = -\frac{e^2\mathrm{H}}{6mc^2}\underset{n}{\overline{\Sigma r^2}} \quad . \quad . \quad . \quad (6)$$

and the magnetic moment per gram-atom is, therefore,

$$\Delta\mu_{\mathrm{A}} = -\mathrm{N}\frac{e^2\mathrm{H}}{6mc^2}\underset{n}{\overline{\Sigma r^2}} \quad . \quad . \quad . \quad (7)$$

where N is Avogadro's number, $6{\cdot}06\times10^{23}$ atoms per gram-atom.

The magnetic moment per unit volume gives the intensity of magnetisation and we have

$$\mathrm{I}=\frac{\rho}{\mathrm{A}}\Delta\mu_{\mathrm{A}} = -\mathrm{N}\frac{\rho}{\mathrm{A}}\frac{e^2\mathrm{H}}{6mc^2}\underset{n}{\overline{\Sigma r^2}} \quad . \quad . \quad . \quad (8)$$

where ρ is the density and A the atomic weight of the substance.

If an atom possesses no intrinsic magnetic moment the gram-atomic susceptibility χ_{A} is given by

$$\chi_{\mathrm{A}}=\frac{\Delta\mu_{\mathrm{A}}}{\mathrm{H}} = -\mathrm{N}\frac{\quad}{6mc^2}\underset{n}{\overline{\Sigma r^2}} \quad . \quad . \quad . \quad (9)$$

or substituting numerical values we obtain

$$\chi_{\mathrm{A}} = -2{\cdot}832\times10^{10}\overline{\Sigma r^2}\ * \quad . \quad . \quad . \quad (10)$$

As a consequence of this equation two points should be carefully noticed:

---

* On calculation from the most recent atomic constants given by Birge the revised value comes out to be 2·832 instead of the former 2·85.

(i) Since the value of the diamagnetic susceptibility arises from the Larmor 'precession' of the electronic orbits which is independent of any thermal variation of the kinetic energy of the atoms, it follows that the diamagnetism should be independent of temperature.

(ii) That diamagnetism is the underlying property for all atoms and molecules. Only if the atom possesses an initial magnetic moment the underlying diamagnetism may entirely be masked by the large value of the magnetic moment and would consequently be incapable of being directly measured.

2. APPLICABILITY OF THE LANGEVIN THEORY OF DIAMAGNETISM

The theory which has been outlined above applies strictly to 'mononuclear' systems, namely to atoms or ions in solids or solutions. The theory cannot be applied directly in a satisfactory manner to the solid state, though in a field of such vast complexity even approximate relationships may open up a vista of valuable information regarding the nature of internal mechanism. Langevin's theory has therefore been applied in case of all sorts of elements and compounds. As illustrations:

(i) It has been shown that the order of the susceptibilities calculated for all elements in the Periodic Table is in agreement with the observed and experimentally obtained values of susceptibilities for these elements. In an atom the mean square radius $\Sigma\overline{r^2}$ of the electronic orbits may range from 0·1 to $1{\cdot}0 \times 10^{-8}$ cm. Substituting the values for the lower and the higher limits and supposing that atomic weight is nearly twice the atomic number, i.e. $n=2$, we get as a rough approximation from Langevin's equation, the following range of susceptibility values for elements:

$$\chi_A = -\frac{2{\cdot}832\times10^{10}}{2}\times(0{\cdot}1\times10^{-8})^2 = -0{\cdot}014\times10^{-6}$$

$$\chi_A = -{}^{2{\cdot}832}\times10^{10}\times(1{\cdot}0\times10^{-8})^2 = -1{\cdot}4\times10^{-6}$$

On reference to Chapter IV these values will be found to be in accord with the order of experimental values. Considering the limits of the original treatment this agreement is remarkable.

(ii) The values for $\sqrt{r^2}$ for H, C, N, etc., calculated from the susceptibilities of these elements, give a value of 1·1, 0·59 and 0·53 A.U. This order is almost the same as that deduced from other evidence.

(iii) It is now well recognised that the chemical similarity of elements is due to their similar electronic configuration. According to Langevin's equation, the value of χ_A is a function of the number of electrons in the atom, and for the case of chemically similar elements, therefore, there should be expected a regular increase in the value of χ_A with atomic number. This is found to be experimentally true when we compare the values of χ_A for Cl, Br, I or S, Te or for Zn, Cd and Hg.

A more convincing way of proving the validity of Langevin's equation was given by Joos. If we consider the argon atom with eighteen electrons, we see that it has the same electronic configuration as the K^+ and Cl^- ions. According to Langevin's theory, in passing through the series Cl^-, A, K^+, the ionic (or atomic) susceptibilities should decrease as a result of the decrease in size of the electronic orbits owing to the increasing nuclear charge. If Z represents the effective nuclear charge, then for orbits characterised by the same quantum numbers

$$r^2 \propto \frac{1}{Z^2}$$

For K^+ and Cl^-, therefore, as a sufficiently close approximation from equation (10), one gets the relation

$$\chi_{K^+} : \chi_{Cl^-} = \frac{1}{19^2} : \frac{1}{17^2}$$

Now χ_M for KCl is $-35{\cdot}0 \times 10^{-6}$, and the values for K^+ and Cl^- on this ratio would therefore be

$$K^+ = -15{\cdot}5 \times 10^{-6}$$
$$Cl^- = -19{\cdot}5 \times 10^{-6}$$

On interpolation the value for argon comes out to be

$$A = -17{\cdot}5 \times 10^{-6}$$

This is in excellent agreement with the experimental values of Hector and Wills[4].

(iv) An extension of Langevin's theory which throws much light on its validity has been proposed by Bhatnagar and R. N. Mathur[5]. Since, according to Langevin's equation, χ_M is a function of the number of electrons and the radii of their orbits, it should be possible to find simple relationship between the values of χ for isomeric electronic molecules and the radii of these molecules. Generalising Langevin's equation, Bhatnagar and Mathur, therefore, gave the following empirical equation:

$$\chi_M = -\frac{e^2 N}{6mc^2} K(r^2) \quad . \quad . \quad . \quad (11)$$

The above equation essentially differs from Langevin's equation in that instead of taking the total number of electrons n we take only a fraction of them K. This fraction K must evidently depend in some way upon the total number of electrons in the molecule. Its numerical value in the case of molecules constituting electronic isomers should therefore be the same. In the following table are given the values of χ_M for some molecules with their radii calculated according to the method proposed by W. L. Bragg on the view-point of closest packing.

TABLE I

VALUES OF K FOR ELECTRONIC ISOMERS

Substance	r in A°	$-\chi_M \times 10^6$ Experimental	$-\chi_M \times 10^6$ Calculated	K
Glycerine . . .	1·502	56·82	57·61	8·96
Aniline . . .	1·595	65·17	64·97	8·96
Methylbenzoate . .	1·754	83·23	82·92	9·46
Phenylacetate . .	1·754	82·69	82·92	9·46
Phenylhydrazine . .	1·648	62·03	63·45	8·2
o-cresol . . .	1·670	65·16	65·16	8·2

It is clear from the above table that the values of K in the case of electronic isomers are the same. As a matter of fact when a larger number of electronic isomers are considered very characteristic relations between K, n and the number of atoms in the molecules are noticeable.

3. DIAMAGNETISM ON QUANTUM MECHANICS

It would not be out of place here to consider briefly the refinements which have been introduced in the theory of diamagnetism from the standpoint of quantum mechanics.

Van Vleck[6] has developed a general theory of dia- and paramagnetism introducing the wave-mechanical ideas. In diamagnetics the theory applies strictly to mononuclear systems only. According to this theory the susceptibility per gram-atom or gram-ion of a diamagnetic substance can be expressed by the relation

$$\chi_M = \underset{\text{(1st Term)}}{Ne^2\ \Sigma\overline{r_k^2}} + \underset{\text{(2nd Term)}}{\tfrac{2}{3}N \sum_{n'\neq n} \frac{m_0(n\,;\,n')}{h\nu(n'\,;\,n)}} \qquad (12)$$

where N = Avogadro's number,

$\overline{r_k^2}$ = time average value of the square of the orbital radius of the kth electron, the summation extending over all electrons in the system,

$m_0(n'\,;\,n)$ = a non-diagonal element of the matrix for the angular momentum of the system,

$\nu(n'\,;\,n)$ = frequency corresponding to n', n transition,

e = electronic charge,

m = the mass of the electron,

and h = the Planck constant.

In most cases the right-hand side term (2) of the equation (12) vanishes as it arises from the part of the magnetic moment perpendicular to the resultant angular momentum and for states in which both L and S are zero, namely for ^1S state of the atom or the molecule. Systems in states other than this are not to be considered on account of their overwhelming paramagnetism. With this restriction the theory reduces itself to

$$\chi_M = -\frac{Ne^2}{6mc^2}\Sigma\overline{r^2}$$

which is the well-known Langevin equation.

It is clear from the above expression that if the values of $\overline{r^2}$ for different quantum orbits be known, the values of χ for any atom can be easily calculated. With the help of the new quantum mechanics, Pauling[7] and Van Vleck[8] have independently derived the following expression for $\overline{r^2}$ for a single electron moving in the field of a nucleus of charge $(Z-s)e$, in an orbit of quantum numbers n and l (cf. Chapter V):

$$r^2 = \frac{a_0^2 n^2}{(Z-s)^2}\left.\frac{5}{2}n^2 - \frac{3l(l+1)-1}{2}\right\} \qquad (13)$$

In this expression $\overline{r^2}$ is given in terms of the radius of the one quantum orbit of hydrogen ($a_0 = 0{\cdot}528 \times 10^{-8}$ cm.).

The only unknown factor in the above expression is s, the screening constant. Adopting the charge distribution conception of the atom, Pauling has estimated its values for different electron groups in atoms and ions containing many electrons and used them to calculate a number of susceptibilities. In Table II Pauling's results, along with those obtained by other methods, are compared with experimental results for inert gases.

Stoner[9] has recently calculated the values of $\overline{r^2}$ in a few cases from Hartree's data[10]. By Hartree's 'self-consistent field' method the charge distribution satisfying the Schrödinger equation can be worked out. For a number of atoms and ions Hartree has given tables and curves showing the charge per unit radial distance as a function of the distance from the nucleus. According to Hartree's notation $\dfrac{dz}{dr}$ is the radial charge density in electrons per unit radial distance. Then

$$\overline{r^2} = \int_0^\infty r^2\left(\frac{dz}{dr}\right)dr \Big/ \int_0^\infty \left(\frac{dz}{dr}\right)dr \quad . \qquad (14)$$

The lower integral is obviously equal to the number of electrons in the atom, and according to equation (10)

$$\chi_A = -2{\cdot}832 \times 10^{10} \int_0^\infty r^2\left(\frac{dz}{dr}\right)dr \quad . \quad . \quad (15)$$

The integral in the above expression can easily be evaluated graphically. From Hartree's $\left(r, \dfrac{dz}{dr}\right)$ curves Stoner has drawn curves for $\left(r^2\dfrac{dz}{dr}\right)$ against r, and the area of this curve gives the value of the integral. For the sake of closer comparison the values for inert gases obtained in this manner are also shown in Table II. Values obtained by Stoner are marked with an asterisk.

Slater[11] has recently published another method of estimating space charge distributions. Adopting for the wave-function of an electron in a symmetrical form the expression

$$\psi = r^{(n^*-1)} e^{-\left(\frac{Z-s}{n^*}\right)r} \quad . \quad . \quad . \quad (16)$$

where n^* is the effective principal quantum number and $(Z-s)$

the effective nuclear charge, Slater arrives at the following expression:

$$\overline{{}^{2}}=\int_0^\infty r^4\,|\,\psi\,|^2\,dr\Big/\int_0^\infty r^2\,|\,\psi\,|^2\,dr$$
$$=(n^*)^2(n^*+\tfrac{1}{2})(n^*+1)/(Z-s)^2 \quad . \quad . \quad (17)$$

Slater's expression has recently been used by Brindley [12] to calculate the diamagnetic susceptibilities of a large number of ions. The values obtained by this method in the case of inert gases are also included in Table II.

TABLE II

THEORETICAL AND EXPERIMENTAL SUSCEPTIBILITIES FOR INERT GASES. $-\chi_A \times 10^6$

Gas	Calculated			Observed	
	Hartree	Pauling	Slater	Wills and Hector	Havens[27]
Helium . .	1·90	1·54	1·68	1·88	1·91
Neon . .	8·81	5·7	5·7	6·66	7·65
Argon . .	25·3	21·5	18·8	18·13	19·23

For helium the calculated values are in fair agreement with the experimental ones, but for neon and argon the agreement is not satisfactory according to the first two methods. Values calculated by Slater's method show better agreement with experiment in all cases.

Angus [13] has introduced a modification in Slater's method of calculation in that while Slater takes the *s* and *p* electrons together in calculating the screening constant, he introduces the refinement of taking them separately. This results in a lowering of the χ values by increasing the effective charges for the *s* electrons, and the concordance is improved for heavier atoms in which case Slater's method yields values which are a bit too high, while it is impaired for the lighter ones.

4. SOME APPLICATIONS OF THE THEORY OF DIAMAGNETISM

It is now possible to deal with the data of Pascal (cf. Chapter IV) in a more rational manner and to assign to some of his conclusions meanings which are capable of physical interpretation in terms of modern theories. On the charge distribution concepts of the atoms by Pauling and on Hartree's 'self-consistent' field theory the diamagnetic susceptibility has been shown to be a good indication of the space charge distribution. In Pascal's work the value of λ for a double bond is given a paramagnetic or a plus value.

On the above concepts the decrease in diamagnetic susceptibility due to an ethylene linkage or a double bond as compared with the ethane configuration or a single bond is to be attributed to a concentration of the electronic charge. In an ordinary single bond each carbon atom constitutes an electronic distribution of the 'inert gas' type, while in a double and a triple bond the two carbon atoms approximate to a single centre for the outer part of the electronic charge. From Pascal's work multiple bonds have in general a paramagnetic effect, or in other words their presence in a compound brings down the value of diamagnetic susceptibility. The multiple bonds represent regions in which two or more nuclei are drawn together and as a result of this the electronic charge is more concentrated, or in terms of the orbital theory the electronic orbits are reduced in area in such regions and so contribute less towards diamagnetism.

A confirmation of this comes from some work of Bhatnagar, R. N. Mathur and Nevgi[14] on the magnetic susceptibilities of organic isomers. Both position and geometrical isomers have been investigated. The results obtained show that there are small but real differences between their susceptibilities. This reality has been established as a result of the use of the delicate

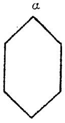
TABLE III

COMPARATIVE SUSCEPTIBILITIES FOR GEOMETRICAL AND POSITION ISOMERS. $-\chi_M \times 10^6$

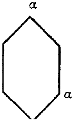
Position Isomers	Molecular Magnetic Susceptibility	Geometrical Isomers	Molecular Magnetic Susceptibility
o-cresyl methyl ether	81·94	Maleic acid	49·71
m-cresyl methyl ether	77·91	Fumaric acid	49·11
p-cresyl methyl ether	79·13		
o-phenetidine	101·1	Chlormaleic acid	67·36
p-phenetidine	95·86	Chlorfumaric acid	67·02
Butyric acid	55·49	Citraconic acid	57·84
Isobutyric acid	57·08	Mesaconic acid	56·98
Butyl bromide	77·14	Elaidic acid	204·8
Isobutyl bromide	79·88	Oleic acid	208·2

Bauer and Piccard method and the magnetic interference balance developed in the course of these investigations. Selected results for the sake of discussion are given in Table III.

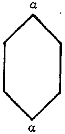
The diamagnetic susceptibilities of these isomers differ in general from each other in the order: ortho$>$ para$>$ meta, normal $<$iso, and the cis$>$ trans variety. There are a number of explanations possible and they have been fully explored in the original paper and found wanting.



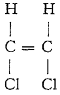
Ortho.



Meta.

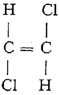


Para.



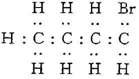
$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ Cl & & Cl \end{array}$$

Cis.



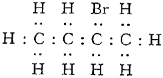
$$\begin{array}{ccc} H & & Cl \\ | & & | \\ C & = & C \\ | & & | \\ Cl & & H \end{array}$$

Trans.



$$\begin{array}{ccccccccc} & & H & & H & & H & & Br \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot \\ H & : & C & : & C & : & C & : & C \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot \\ & & H & & H & & H & & H \end{array}$$

I. Butyl bromide.



$$\begin{array}{ccccccccccc} & & H & & H & & Br & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ H & : & C & : & C & : & C & : & C & : & H \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ & & H & & H & & H & & H & & \end{array}$$

II. Isobutyl bromide.

The interpretation of these results on the concept of change in the radii of the electronic orbits owing to changes in the effective electronic charge is a logical consequence.

Consider a particular case, say of butyl and isobutyl bromide:

When Br and C combine there are two shared electrons as Br requires one extra electron to complete the inert gas configuration. These shared electrons would move in orbits under the influence of two centres of forces, the bromine and carbon nuclei, and the dimensions of these orbits will evidently depend upon the effective positive charges on the two nuclei. Denoting the carbon atoms with which the bromine atoms are linked in formula I and II by C_1 and C_2 respectively, we see that both C_1 and C_2 have got six shared electronic orbits; but the three nuclei (two carbon and one hydrogen) with which C_2 is linked have got a greater positive charge than those (two hydrogen and one carbon) linked with C_1 and it is therefore clear that for combination with other atoms the effective positive charge of C_2 will be less than that of C_1. Similarly, if Br_1 (Br in I) and Br_2 (Br in II) are taken into consideration it is seen that Br_2 is surrounded by a greater number of positive nuclei than Br_1. It is a well-known fact that the presence of such positive nuclei around any nucleus decreases its effective positive charge. The effective positive charge on Br_2, therefore, will also be less than that on Br_1. As previously mentioned, the dimensions of the shared electronic orbits between C_2 and Br_2 will therefore be greater than the dimensions of the similar orbits between C_1 and Br_1; and consequently, according to the electronic theories of diamagnetism, isobutyl bromide should be more diamagnetic than butyl bromide.

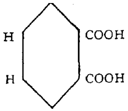
Tertiary Compounds.—The magnetic behaviour of tertiary compounds can also be similarly explained. The corresponding carbon atom, say C_3, would have six shared electrons with the three carbon atoms around it. Hence the positive charges on the three nuclei with which it is associated would be still greater. Its effective positive charge will therefore be less, and tertiary compounds should be still more diamagnetic, which is actually the case.

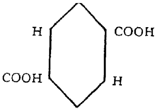
Ortho, Meta and Para Isomers.—The difference between the magnetic susceptibilities of ortho-, meta- or para-position isomerides can also be similarly explained. For convenience of reference the carbon atoms in the benzene ring may be denoted by C_1, C_2 . . . C_6. Unlike the case of primary, secondary and tertiary isomerides, the carbon atoms in the benzene ring are all initially alike, and there is only one mono-substitution product, but when a hydrogen atom associated with any of the carbon atoms, say C_1, has been substituted, say, by a bromine atom, the remaining carbon atoms do not remain all exactly alike. Being nearest, the decrease in the effective positive charges of C_2 and C_6 for combination with other atoms will be maximum. Moreover, in the ortho position the two substituent groups are nearest together. Their effective positive charges, therefore, will be least in this position, and hence, according to what has been given before, the ortho should be more diamagnetic than the meta or para-isomerides. This actually is the case.

The Cis and Trans Isomers.—It now remains to show why the cis should be more diamagnetic than the trans variety. The formulae for the cis and trans and the corresponding ortho and para compounds are given below:

H—C—COOH H—C—COOH

H—C—COOH COOH—C—H





It is clear from the above formulae that if in place of the benzene ring the ethylene bond is substituted the ortho and para shall change into the cis and trans forms. By precisely similar reasoning, therefore, it can be shown that the cis would be more diamagnetic than the trans isomerides.

5. THE MOLECULAR SUSCEPTIBILITY OF HYDROGEN ON THE NEW MECHANICS

The new mechanics provides a very gratifying theoretical justification for the value of χ_M for hydrogen deduced from organic compounds by Pascal's additivity principle. Van Vleck,[15] in considering diamagnetism from the standpoint of quantum mechanics, supposes the atoms to be in singlet S states. Neglecting the second term in equation (12) for reasons given before, he restores the classical formula of Langevin according to which

$$\chi_M = -\frac{Ne^2}{6mc^2}\Sigma\overline{r^2} = -2{\cdot}832\times10^{10}\Sigma\overline{r^2} \qquad (18)$$

On the old quantum theory the value for $\overline{r^2}$ was given by

$$\overline{r^2} = a_0{}^2\frac{n^2}{Z^2}\left(\tfrac{5}{2}n^2 - \tfrac{3}{2}k^2\right) \qquad (19)$$

where $a_0 = 0{\cdot}528\times10^{-8}$ and refers to the radius of the innermost $(1-1)$ orbit in hydrogen.

Substituting the value of $\overline{r^2}$ so obtained in equation (18), which is identical in form for both the theories, the old theory yields for hydrogen,

$$\chi_M = -2{\cdot}832 \times 10^{10} \times a_0^2 (\tfrac{5}{2}n^2 - \tfrac{3}{2}k^2)\frac{n^2}{Z^2}$$

$$= -2{\cdot}832 \times 10^{10} \times (0{\cdot}528 \times 10^{-8})^2$$

$$= -0{\cdot}79 \times 10^{-6} \quad . \quad . \quad . \quad . \quad (20)$$

On the new quantum mechanics the value of $\Sigma\overline{r^2}$ for hydrogen-like atoms is given by

$$\left(\frac{h^2}{4\pi^2 Ze^2 m}\right)^2 [\tfrac{5}{2}n^4 - \tfrac{3}{2}n^2 l(l+1) + \tfrac{1}{2}n^2] \quad . \quad . \quad (21)$$

Substituting these values in equation (18) we get

$$\chi_M = -2{\cdot}832 \times 10^{10}\left(\frac{h^2}{4\pi^2 Ze^2 m}\right)^2 [\tfrac{5}{2}n^4 - \tfrac{3}{2}n^2 l(l+1) + \tfrac{1}{2}n^2]$$

$$= -0{\cdot}79 \times 10^{-6}\left[\frac{5n^4 - 3n^2 l(l+1) + n^2}{2Z^2}\right] \quad . \quad . \quad (22)$$

For the normal state of hydrogen $n=1, l=0, Z=1$. Substituting these values in (22) we get

$$\chi_M = -0{\cdot}79 \times 10^{-6} \times 3 = -2{\cdot}37 \times 10^{-} \quad . \quad (23)$$

The indirect value for the diamagnetic susceptibility obtained by Pascal from his additivity method was $-3{\cdot}05 \times 10^{-6}$, which when suitably corrected for water yields for it the value $-2{\cdot}93 \times 10^{-6}$. This value does not differ much from the value in (23). A better agreement is not expected, as the analysis of compounds by assuming additivity rules does not necessarily furnish the atomic properties.*

6. Diamagnetism of Polyatomic Molecules and Argument for the Constitutive Correction Factor in Pascal's Additivity Law

According to Van Vleck[15], when a polyatomic molecule has a spin quantum number zero, the commonest value for even molecules, the susceptibility is given by the expression (Eq. 12),

---

* Some recent accurate measurements on organic compounds by Bhatnagar, Mitra and Tuli, using the Magnetic Interference Balance, give for hydrogen, $\chi_M = -2{\cdot}68 \times 10^{-6}$. This gives a better agreement than Pascal's value.

$$\chi_{\mathrm{M}} = -\underbrace{\frac{\mathrm{N}e^2}{6mc^2}\Sigma\overline{r^2}}_{\text{(1st Term)}} + \underbrace{\tfrac{2}{3}\mathrm{N}\Sigma_{n'\neq n}\frac{|m^0(n\,;n')|^2}{h\nu(n'\,;n)}}_{\text{(2nd Term)}}$$

The material is diamagnetic or paramagnetic depending on whether the first or the second term of the above equation is greater. In nitrous oxide (N_2O), for example, the first term is greater and the substance is known to be diamagnetic. There are some substances in which the second term is greater; such substances exhibit a feeble paramagnetism independent of temperature, e.g. $KMnO_4$ and complex ions.

In considering Van Vleck's equation the second part of the expression was neglected in Section 3, as the paramagnetic contribution by atoms in singlet *S* states was considered to be negligible. In dealing with diatomic and polyatomic molecules the same simple consideration ceases to be applicable. Closely connected with it is the fact that even on classical considerations the Langevin formula applies strictly to monoatomic molecules, because the validity of Larmor's theorem is confined to mononuclear systems. Since the second term in Van Vleck's formula is inherently positive, it follows that the Langevin formula can at best be an upper limit to the value of diamagnetism. In the case of molecules the mean square radii deduced from this formula will tend to give too high a value. This may provide an explanation as to why most of the constitutive correction constants deduced by Pascal on additivity principle are found to have a paramagnetic value (*vide* Table V, Chapter IV). But the fact, however, that reasonable estimates of orbital radii can be obtained for simpler molecules by the application of the Langevin formula shows that most often the second term must be of a secondary order compared to the first.

Van Vleck, from calculations of himself and Miss Frank[16] and of Wang[17], has computed that in the case of hydrogen molecule the first term of the equation (12) comes out to be $-4{\cdot}71\times10^{-6}$ and the second term to be $+0{\cdot}51\times10^{-6}$ per mol. Hence the computed molar susceptibility of H_2 is $-4{\cdot}20\times10^{-6}$. The experimental values are $-3{\cdot}94\times10^{-6}$ (Wills and Hector) and $-3{\cdot}99\times10^{-6}$ (Sone). The inclusion of second term distinctly improves the agreement. The second term here is about 10 per cent. of the first, but it is likely that in molecules which depart more from axial symmetry its value may be larger.

7. TEMPERATURE AND DIAMAGNETIC MOLECULES

Although diamagnetism has been shown to be independent of temperature, there are a large number of diamagnetic substances which have been found to be influenced by temperature. The most interesting case is that of water and some of the aliphatic alcohols which have been investigated by Johner[18] and by R. N. Mathur[19]. In these cases the diamagnetic susceptibility has been found definitely to increase with temperature.

TABLE IV

VARIATION OF DIAMAGNETIC SUSCEPTIBILITY WITH TEMPERATURE

Substance	$-\chi \times 10^6$	% Change	Range of Temperature °C.
Water	0·721 – 0·726	0·69	30°–75°
Isobutyl alcohol . . .	0·810 – 0·815	0·72	30°–75°
Butyl alcohol	0·800 – 0·805	0·70	30°–75°
Propyl alcohol . . .	0·771 – 0·776	0·77	30°–75°
Isopropyl alcohol . .	0·788 – 0·791	0·50	30°–60°

It has to be noted that out of a large variety of substances examined only water and a few aliphatic alcohols were found to possess the remarkable property of showing an increase in diamagnetism due to temperature.

Substances of this type are known to show large variations of molecular association and dissociation with temperature and it appears that the change in magnetic properties may be intimately connected with these changes.

The electrically polarised molecules such as water, propyl, isopropyl, butyl, isobutyl alcohols, etc., ought to have, on Van Vleck's theory, an additional paramagnetic moment whose value should decrease with temperature. The diamagnetic susceptibility of such a molecule should, therefore, show an increase with rise of temperature. Johner has tried to quantitatively test this view on water molecules, but the observed increase between 0° and 100° was found to be ten times greater than what could be accounted for on the polarisation hypothesis. From this it is clear that a large part of increase is due to change in molecular association and only a small part of this effect can be ascribed to the polarisation factor.

Table V contains a brief résumé of the investigations on the reverse phenomenon, namely that of decrease in diamagnetism with temperature.

TABLE V

VARIATION OF DIAMAGNETIC SUSCEPTIBILITY WITH TEMPERATURE

Substance	$-\chi \times 10^6$	% Change	Range of Temperature. °C.
Phenyl iodide	0·4700 – 0·4620	1·7	30 to 70
o-iodotoluene	0·5145 – 0·5051	1·8	30 to 70
m-iodotoluene	0·5152 – 0·5065	1·7	30 to 70
N-propyl iodide	0·4958 – 0·4834	2·5	30 to 70
Ethyl iodide	0·4488 – 0·4356	2·9	15 to 55

It may be noted that the above compounds contain iodine, and the presence of this element may be responsible for the temperature effect.

The observations of R. N. Mathur[19] that meta-cresol and nitrobenzene show change of susceptibility with temperature lack confirmation. Recently Cabrera and Fahlenbrach[20] have reported that they could not detect any change except near the boiling or melting point. Bhatnagar, Nevgi and Khanna[21] confirm Cabrera and Fahlenbrach and have given reasons for the conflicting results obtained before.

8. DIAMAGNETIC SUSCEPTIBILITIES OF IONS

In our treatment of diamagnetism in a previous section of this chapter it has been clearly shown that the ideal substances for testing the various theories are the monoatomic gases. Surprisingly interesting conclusions have been drawn from solutions of salts containing ions, and from solid salts which are definitely known to be ionic. Reference has already been made to the work of Joos[22] in this connection, who calculated the susceptibilities of the K^+ and Cl^- ions on the assumption that the linear dimensions of the electronic system $(\overline{r^2})$ are inversely proportional to the nuclear charge and that the susceptibility therefore varies inversely as the square of the charge. The subject has been considerably extended by Ikenmeyer[23], whose results indicate that in about twenty salts studied by him there was no perceptible interaction between the ions, and the susceptibility of the dissolved salts could be calculated in a simple manner according to the equation

$$\chi = C_s\chi_s + \chi_w - C_s\chi_w \text{ (cf. Chapter III, Section 8)}$$

The molecular susceptibilities so calculated were plotted against the sum of the nuclear charges of the ions forming the molecule. These results were utilised to evaluate the relative contribution of the anion and kation to the susceptibility of a particular salt in a manner identical with that of Joos. Further, a series of ionic susceptibilities was determined by comparison with different salts containing the same anion or kation. For example, Ikenmeyer found that the molecular diamagnetic susceptibility of caesium iodide was $-95{\cdot}0 \times 10^{-6}$ and the relative susceptibility contributions of the anion and the kation following the Joos method came to

$$Cs^{+} = -45{\cdot}75 \times 10^{-6}$$
$$I^{-} = -49{\cdot}25 \times 10^{-6}$$

From the experimentally determined values of the molecular susceptibilities and gram ionic susceptibilities (χ_{ion}) of the I^{-} and the Cs^{+} ions as standards, the values (χ_{ion}) for a number of other ions were calculated. Some of his results are shown in the following table.

TABLE VI

SUSCEPTIBILITY PER GRAM ION. (IKENMEYER)

Ion	$\chi_{\text{ion}} \times 10^6$	Ion	$\chi_{\text{ion}} \times 10^6$	Ion	$\chi_{\text{ion}} \times 10^6$
Li^{+}	$-4{\cdot}0$	Mg^{++}	$-4{\cdot}5$	F^{-}	$-13{\cdot}9$
Na^{+}	$-10{\cdot}4$	Ca^{++}	$-11{\cdot}0$	Cl^{-}	$-20{\cdot}4$
K^{+}	$-16{\cdot}9$	Sr^{++}	$-25{\cdot}4$	Br^{-}	$-34{\cdot}8$
Cs^{+}	$-45{\cdot}75$	Ba^{++}	$-39{\cdot}9$	I^{-}	$-49{\cdot}25$

In addition to this method reference has already been made to the theories of Pauling and Van Vleck from which the susceptibilities of helium, neon and argon-like ions could be predicted. The agreement between the calculated and experimental values is satisfactory for simpler ions. Stoner, using Hartree's method, has also calculated the susceptibilities of a large number of ions. A comparison of the experimental and calculated values is given in Table VII.

The agreement between the calculated and the experimental results established the justification of the assumptions made by these authors that every electronic orbit takes part in the diamagnetic effect.

Mention may also be made of the view which has been put forward by Gray and Farquharson[24], who consider the diamagnetic changes brought about by the coming closer together

TABLE VII

GRAM IONIC SUSCEPTIBILITIES. $-\chi_{\text{ion}} \times 10^6$

Ion	Theoretical Values			Experimental Values			
	Pauling	Stoner (Hartree)	Slater	Hocart[25]	Pascal	Kido[26]	Ikenmeyer
Li^+	0·63	0·70	0·67	..	..	1·6	..
Na^+	4·2	5·47	4·2	8·2±0·9	7·6	7·6	10·4
K^+	16·7	17·64	14·4	16·5±0·9	16·0	13·6	16·9
Rb^+	35·0	30·12	25·8	..	24·3	27·2	31·3
Cs^+	55·0	..	39·5	..	38·0	41·0	45·75
Mg^{++}	3·2	4·3	3·2	5·15±2·6	8·0	4·3	4·5
Ca^{++}	13·3	13·4	11·4	10·6±1·8	12·2	6·5	11·0
Sr^{++}	28·0	..	21·5	18·9±1·6	20·6	15·6	25·4
Cl^-	29·0	40·39	25·8	23·1±0·6	23·1	22·1	20·4
Br^-	54·0	..	40·1	33·9±1·2	34·7	34·7	34·8
I^-	80·0	..	59·8	49·5±1·7	49·8	53·2	49·25

of the separate ions in two steps, firstly the formation of the molecule and secondly the formation of a single 'merger atom' by an imaginary forced merging of the ionic nuclei. Thus K^+ and Cl^- first give the molecule KCl and then the merger atom Kr. A diatomic molecule on this view has three nuclei—two real and one virtual. When such a molecule is being formed, it is considered that the virtual nucleus assumes control over certain of the electrons originally controlled by only one or the other of the two real nuclei, and along with this there is the development of weak paramagnetism. A number of examples have been given by these authors, but it remains to be seen whether the quantum mechanics will be able to give a quantitative meaning to the 'merger' atom.

From what has been said in this chapter it is clear that much work remains to be done in this field, for we are still far from the fullest interpretation of the diamagnetism of the molecules. For example, in the theories so far discussed, the crystalline structure effects which certainly do play some part have not been considered at all. There is also no provision in the theories considered for the change on melting which Oxley and others noticed. These facts have been discussed at greater length in a later chapter on the magnecrystallic effect. The applications of the ideas of quantum mechanics to the subject of diamagnetism are also in their infancy and there is a very extensive field of investigation which lies unexplored in this direction.

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CHAPTER VII

PARAMAGNETISM

It has been shown in the last chapter how the diamagnetic properties of an element may be accounted for on the electronic theory by assuming that in the atom of a diamagnetic substance the electronic orbits are so disposed that their resultant magnetic moment is zero at points outside the atom. In the theory of paramagnetism as originally given by Langevin[1], the assumption is made that the electronic orbits are such that the rotating electrons produce a resultant effect at points outside the atom, with the consequence that the atom as a whole has a resultant magnetic moment.

1. THEORY OF PARAMAGNETIC GASES

For the sake of simplicity we may consider the case of a paramagnetic gas whose molecules behave as small magnets having a moment μ. We assume that in the absence of an external magnetic field the gas is in a state of thermal equilibrium, with molecules distributed at random in all directions in accordance with the Maxwell-Boltzmann law. On this law it is possible also to calculate, as a statistical probability, the number of molecules which take up a particular orientation in a magnetic field. The distribution, when equilibrium has been established, will be such that the number of molecules contained in a unit solid angle, with their axes pointing in a direction α with respect to an impressed field H, will be proportional to $e^{-\frac{E}{kT}}$, where k is the Boltzmann constant, T the absolute temperature and E the potential energy.

For a small molecular magnet of moment μ the potential energy in a magnetic field H will be given by

$$E = -\mu H \cos \alpha$$

where α is the angle which the molecular axis makes with the field direction, and consequently

$$e^{-\frac{E}{kT}} = e^{\frac{\mu H \cos \alpha}{kT}}$$

The number dn of molecules with axes lying within a solid angle $d\omega$ and making an angle α with the direction of the field is given by

$$dn = \mathrm{K}e^{\frac{\mu\mathrm{H}\cos\alpha}{k\mathrm{T}}}d\omega \quad . \quad . \quad . \quad . \quad (1)$$

where K is a constant.

The molecular axes will be symmetrically distributed about the direction of the field and the solid angle $d\omega$ will be that contained between two cones with their semi-vertical angles equal to α and $\alpha + d\alpha$, so that $d\omega = 2\pi \sin\alpha d\alpha$.

Substituting this value in equation (1), we have

$$dn = \mathrm{K}e^{\frac{\mu\mathrm{H}\cos\alpha}{k\mathrm{T}}} 2\pi \sin\alpha d\alpha \quad (2)$$

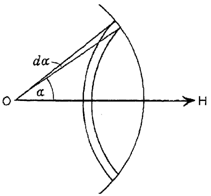

FIG. 33.

The magnetic moment due to dn molecules at an angle α will have a component in the direction of the field such that the resolved molecular magnetic moment will be

$$\mathrm{K}e^{\frac{\mu\mathrm{H}\cos\alpha}{k\mathrm{T}}} 2\pi \sin\alpha . d\alpha . \mu\cos\alpha \quad (3)$$

and since α may take values between 0 and π we have for the mean effective magnetic moment, from equation (3)

$$\mathrm{M} = n\bar{\mu} = \int_0^\pi \mathrm{K}e^{a\cos\alpha} 2\pi \sin\alpha d\alpha . \mu\cos\alpha \quad . \quad . \quad (4)$$

and for n, from equation (2)

$$= \int_0^\pi \mathrm{K}e^{a\cos\alpha} 2\pi \sin\alpha d\alpha \quad . \quad . \quad . \quad (5)$$

where a has been put for $\frac{\mu\mathrm{H}}{k\mathrm{T}}$.

The integrals can be evaluated by putting $x = \cos\alpha$, so that $dx = -\sin\alpha d\alpha$, and

$$n = 2\pi\mathrm{K}\int_{-1}^{+1} e^{ax}dx$$

$$\frac{2\pi\mathrm{K}}{a}(e^a - e^{-a}) = \frac{4\pi\mathrm{K}}{a}\sinh a \quad . \quad . \quad . \quad (6)$$

and
$$\begin{aligned} M=\bar{\mu}n &= 2\pi\mu K\int_{-1}^{+1} xe^{ax}dx \\ &= 2\pi\mu K\left\{\left[\frac{xe^{ax}}{a}\right]_{-1}^{+1}-\left[\frac{e^{ax}}{a^2}\right]_{-1}^{+1}\right. \\ &= 2\pi\mu K\left\{\frac{1}{a}(e^{a}+e^{-a})-\frac{1}{a^2}(e^{a}-e^{-a})\right. \\ &= 2\pi\mu K\left\{\frac{2}{a}\cosh a-\frac{2}{a^2}\sinh a\right\} \qquad . \quad . \quad (7) \end{aligned}$$

From equations (6) and (7) we have

$$\frac{M}{\mu n}=\frac{\bar{\mu}}{\mu}=\coth a-\frac{1}{a} \qquad . \quad . \quad . \quad . \quad (8)$$

That is, the effective magnetic moment is equal to

$$\bar{\mu}=\mu\left(\coth a-\frac{1}{a}\right)=\mu L(a)$$

where $L(a)$ is called the 'Langevin function'. The term $\coth a-\frac{1}{a}$ can be expanded in the exponential form giving

$$\frac{\bar{\mu}}{\mu}=\frac{a}{3}-\frac{a^3}{45}+\frac{2a^5}{945}-\ldots \text{ etc.} \qquad . \quad . \quad . \quad (9)$$

If a be very small so that the third power can be neglected compared to a, we get, as an approximation,

$$\frac{\bar{\mu}}{\mu}=\frac{a}{3}=\frac{\mu H}{3kT} \qquad . \quad . \quad . \quad . \quad (10)$$

(It can be easily calculated that even with highly paramagnetic substances and fields up to 20,000 gauss at ordinary temperatures the above approximation is sufficiently correct.)

Since the intensity of magnetisation is defined as magnetic moment per unit volume we may put

$$\frac{I}{I_s}=\frac{a}{3}=\frac{\mu H}{3kT} \qquad . \quad . \quad . \quad . \quad (11)$$

where I is the intensity of magnetisation per unit volume and I_s the saturation value of I corresponding to the condition when all the molecules are in alignment with the magnetising field.

Also, if N_v be the number of molecules per unit volume, $I_s = \mu N_v$ and κ the volume susceptibility is given by

$$\kappa = \frac{I}{H} = \frac{N_v \mu^2}{3kT} \quad . \quad . \quad . \quad (12)$$

For the mass susceptibility

$$\chi = \frac{\kappa}{\rho} = \frac{N_v}{\rho} \cdot \frac{\mu^2}{3kT} = \frac{N_m \mu^2}{3kT} \quad . \quad . \quad . \quad (13)$$

where N_m is the number of molecules per gram of the gas.

Further, for a gram-molecule of the gas, if N is Avogadro's number, $N\mu$ is the saturation magnetic moment and denoting it by σ_0, we get from equation (10)

$$\frac{\sigma}{\sigma_0} = \frac{a}{3}$$

where σ is written for the effective gram-molecular magnetic moment.

Since $\frac{a}{3} = \frac{\mu H}{3kT} = \frac{N\mu H}{3NkT} = \frac{\sigma_0 H}{3RT}$, where R is the gas constant, we get

$$\sigma = \frac{\sigma_0^2 H}{3RT} \quad . \quad . \quad . \quad . \quad (14)$$

Hence the gram-molecular susceptibility

$$\chi_M = \frac{\sigma_0^2}{3RT} \quad . \quad . \quad . \quad (15)$$

or

$$\chi_M T = \frac{\sigma_0^2}{3R} = \text{constant} \quad . \quad . \quad . \quad (16)$$

which is the well-known Curie law as first obtained experimentally by Curie for oxygen and other paramagnetic substances. The constant in equation (16) is usually called the Curie constant, and on the Langevin theory it acquires the value

$$C_M = \frac{{}^{2}}{3R} \quad . \quad . \quad . \quad . \quad (17)$$

For the saturation magnetic moment

$$\sigma_0 = \sqrt{3RC_M} \quad . \quad . \quad . \quad (18)$$

which gives a method for determining σ_0 from susceptibility measurements in low fields.

In the above deduction of the paramagnetic theory use has been made of the laws of the kinetic theory of gases, and consequently we may expect the theory to be applicable only to the gaseous state or to those conditions where the gas laws are found to hold good, viz. the dilute solutions.

A number of experimental facts deduced from Curie's and later work show that in many cases the paramagnetic susceptibilities vary inversely as the absolute temperature. In such cases, since the above formula holds, it appears that the mutual magnetic influence of molecules is negligible.

2. Paramagnetic Theory of Solids

In general, to account for the mutual action of molecules upon each other in the case of solids, suitable modification may be introduced in the Langevin equation for paramagnetic gases. It has to be recognised here that a paramagnetic molecule in a magnetic field is under the influence of two opposing forces: (i) the influence of the impressed field, which tends to set all the molecular magnets in perfect alignment with the field direction, and (ii) the influence of the kinetic energy of the molecules, which tends to give the molecular axes a perfectly random distribution. The factor RT in the expression $\sigma=\frac{\sigma_0{}^2H}{3RT}$ is proportional to the kinetic energy of the molecule, and it is due to this that a limit is placed on the extent to which the molecular axes are able to orientate in the direction of the applied field. In solids, however, the closer proximity of the molecules, as also the structural forces like those of the crystalline form, become operative in hindering the free orientations. The effect of these factors could be of a nature similar to that of a change in the kinetic energy and it should be possible to account for it by adding an equivalent kinetic energy term Ω to RT in the paramagnetic equation for gases.

From equation (15) we can get for the corrected equation

$$\chi_M=\frac{\sigma_0{}^2}{3(RT+\Omega)} \quad . \quad . \quad . \quad (19)$$

or writing $\Omega=R\Delta$, where Δ is a positive constant and independent of temperature, the above equation becomes

$$\chi_M=\frac{}{3R(T+\Delta)}$$

or
$$\chi_M(T+\varDelta)=\frac{\sigma_0^2}{3R} \quad . \quad . \quad . \quad (20)$$

The equation (20) is due to Onnes and Perrier[2] and was found by them to be satisfied by a number of solid substances at low temperatures. The scope of this theory has recently been enlarged by the contributions of Weiss, who has extended it to explain the behaviour of ferromagnetics as well.

3. INTRINSIC MOLECULAR FIELD—CURIE-WEISS LAW

Weiss[3] sought to explain the deviations from the simple Curie law by assuming the existence of a molecular field within the solid, whether para- or ferromagnetic. The molecular field H_i was further assumed to be proportional to the intensity of magnetisation, i.e. $H_i \propto I$ or $H_i = nI$ where n is a constant.

Hence the actual field is the sum of the external magnetic field H_e and internal molecular field H_i. That is

$$\begin{aligned} H &= H_e + H_i \\ &= H_e + nI \end{aligned}$$

Substituting this value for H in the paramagnetic equation (14), we have

$$\frac{\sigma}{\sigma_0}=\frac{\sigma_0}{3RT}(H_e+nI) \quad . \quad . \quad . \quad (21)$$

If ρ is the density of the substance, and M its molecular weight, $I=\frac{\rho\sigma}{M}$ where σ, as before, is the gram-molecular moment, and we have

$$\frac{\;}{\sigma_0}\quad\frac{\sigma_0}{3RT}\left(H_e+\frac{n\rho\sigma}{M}\right)$$

and for the gram-molecular susceptibility

$$\chi_M=\frac{\;}{H}=\frac{\sigma_0^2}{3R(T-\varDelta)}-\frac{\;_M}{T-\varDelta} \quad . \quad . \quad (22)$$

where
$$\varDelta=\frac{n\rho\sigma_0^2}{3RM}-\frac{n\rho}{M}C_M$$

The relation $\chi_M(T-\varDelta)=C_M$* is known as Curie-Weiss law, and $\varDelta$ is called the Curie temperature or simply Curie point.

The Curie-Weiss relation may be taken to mean that due to the presence of the internal molecular field the susceptibility varies inversely as the excess of temperature over a certain critical value $\varDelta$ of temperature. In the case of ferromagnetic substances, the Curie temperature is positive and corresponds to the point at which the ferromagnetic property changes to paramagnetism. For paramagnetics Δ is usually small and may be positive or negative.

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* It is more usual to write the equation as $\chi_M\ (T+\Delta)=C$ for low temperatures.

The Curie point may be conveniently determined by $\frac{1}{\chi}$, T curve from which the value for Δ can be read off as the intercept on the T-axis.

4. THE WEISS MAGNETON AND THE *p*-VALUES

An important contribution which Weiss [4] made to the earlier magnetic theory was the introduction of a unit of magnetic moment called the Weiss magneton. The magneton was sought to be regarded as a fundamental unit of magnetic moment in somewhat the same sense as the electron and other physical units. It was contended that all the values of molecular (or atomic) moments were multiples of the Weiss magneton. From his observations Weiss found that for a gram-molecule the magneton should have a value

$$\mu_w = 1123{\cdot}5 \text{ gauss} \times \text{cm. per mole}$$

As discussed previously in Chapter V, Section 15, the theoretical unit of magnetic moment is the 'Bohr magneton' for which the value for a gram-molecule was given as

$$\mu_B = 5564 \text{ gauss} \times \text{cm. per mole}$$

which is almost five times the Weiss unit.

Although no theoretical significance now attaches to the Weiss magneton it is still sometimes convenient to express the experimental values of magnetic moments in terms of this unit.

For the number p of Weiss magnetons in a gram-molecule of the substance we have

$$p = \frac{\sigma_0}{1123{\cdot}5} = \frac{\sqrt{3RC_M}}{1123{\cdot}5} = 14{\cdot}06\sqrt{C_M} \quad . \quad . \quad (23)$$

The expression $\chi_M = \frac{C_M}{T}$ holds over a wide range of temperatures for paramagnetics in dilute solutions. In solids and in case of ferromagnetics above the Curie point the generalised Weiss expression is utilised for calculating p.

In order to determine paramagnetic moments from solutions of paramagnetic salts, account has to be taken of the diamagnetism of the constituent ions and the solvent. For solutions in water the measured mass susceptibility χ is given by

$$\chi = C_s\chi_s + \chi_w - C_s\chi_w \text{ (Chapter III, Section 8).}$$

From a knowledge of χ, χ_w and C_s the value of χ_s can be found from which the χ_M of the solute can be deduced. To obtain the value of Fe^{+++} in $FeCl_3$, for example, it is necessary to correct for the diamagnetism of the chloride ion, the value for which may be obtained from Pascal's data. Many authors have found corrections for anions unnecessary as it can be seen *a priori* that these corrections are negligible for most paramagnetic substances.

In order to determine the Weiss magneton number all that is now needed is a study of the paramagnetic property at three or more temperatures. If a linear relation between $1/\chi$ and T is found to hold, Curie's constant C_M can be deduced from the simple relation $\chi_M = \frac{C_M}{T}$ and from this p the Weiss magneton number can be computed from the relation $p = 14{\cdot}06\sqrt{C_M}$. If the Curie law is not obeyed and the Weiss law $\chi_M = \frac{C_M}{T - \Delta}$ represents the state of affairs, the experimental determination of Δ becomes an important problem as it is capable of giving useful information regarding the magnitude of the internal molecular field.

5. p-VALUES AND THE NATURE OF SOLUTIONS

Much valuable information regarding the nature of physical and chemical changes which take place in the process of solution has been brought to light from investigations on the magnetic properties of solutions themselves. The solutions which have been studied *in extenso* consist mostly of simple compounds of the first transition group (Ca—Cu). In dilute solutions the Curie law is generally obeyed. Concentration seems to have an effect on the value of the Weiss magneton number, and in such cases, where concentrations have marked effect, complex formation resulting in the production of more than one type of magnetic carriers has to be postulated. Generally, however, while calculating ionic moments, it is assumed that the ions which exhibit paramagnetism are of one kind. If however each molecule acts as a carrier of n independently orientating magnets of moments $\frac{\sigma_1}{N}, \frac{\sigma_2}{N} \dots \frac{\sigma_n}{N}$ (N being Avogadro's number) and corresponding to $p_1, p_2, p_3 \dots p_n$ Weiss magnetons, then from the relation (Equations 14, 15 and 16)

$$\frac{\sigma}{H}=\chi_M \quad \frac{\sigma_0^2}{3RT}$$

we have, $\sigma_0 \quad \Sigma_n\sigma_n^2$ and $p^2=\Sigma_n p_n^2$

and $$p^2=\frac{1}{n}(n_1p_1^2+n_2p_2^2+n_3p_3^2+ \dots)$$

where $n_1, n_2 \dots$ are the relative numbers of ions and $n=n_1+n_2+\dots$

The most notable work on solutions has been carried out by Weiss and his pupils, by Cabrera[5], Bauer and Piccard[6], and Bruins[7], and latterly by Chatillon, Freed, and Fahlenbrach[8].

Some of the more important results are summarised in Table I.

The striking colour changes red $\rightleftharpoons$ blue of cobalt chloride solutions have drawn considerable interest. Besides the hydration theory, the help of the ionic theory has been invoked by Ostwald and that of the theory of double-salt formation by Engel[9] in order to explain their behaviour.

In 1902 Donnan and Bassett[10] explained the colour changes on the view that red kations (Co^{++}) are present in the red solution and blue anions $CoCl_4''$ or $CoCl_3''$ are present in the blue solution. According to Hill and Howell[11] cobalt salts are red or blue according as the cobalt atom is surrounded by four or six groups. The magnetic properties of the cobalt salts have also been studied from this standpoint by many workers. Bhatnagar and Kapur[12] have examined the results obtained by them for aqueous solutions and HCl solutions of $CoCl_2$ with those of Chatillon for $CoCl_2, 6H_2O$ in HCl solutions. One is immediately struck by the remarkable fact that in all cases examined by them the value of p falls from 25 to a figure between 22 and 24. This fall in the value of p is not due to the production of the anhydrous $CoCl_2$ as suggested by Lewis,[13] Jones and Bassett[14] or to $CoCl_2, 2H_2O$ as suggested by Hartley[15], as the value of p for both these salts is approximately 25, the usual value for cobalt salts. The addition of HCl evidently results in

TABLE I

p-VALUES FOR SOLUTIONS

Ion	Atomic Number of Ion	Salts Investigated	Value of p	Name of Investigator	Remarks
Ni^{++}	26	$NiSO_4$, $NiNO_3$, $NiCl_2$	16·05 16·03	Bruins, Weiss	From 0·6 to 22 per cent for $NiCl_2$ p is constant within 0·4 per cent
Co^{++}	25	$CoSO_4$, $CoCl_2$	Varies between 22, 23, 24, 25 and 26	Trümpler, Cabrera, Chatillon, Bhatnagar and Kapur	The case of cobalt is discussed in detail below
Fe^{+++}	23	$FeCl_3$, $Fe(NO_3)_3$, $Fe_2(SO_4)_3$	27 to 29	Cabrera and Moles	At lower concentrations $p=27$; at higher 29. In ferric pyrophosphate $p=25$; $p=29$ is generally accepted
Fe^{++}	24	$FeSO_4$(0·37 to 20·7 per cent) $FeSO_4(NH_4)_2SO_4$ (0·25–17·5 per cent)	26·59 26·44	Weiss and Frankamp „	Almost constant values of p are obtained
Cu^{++}	27	$CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$ and other salts	9·6	Mlle. Jacobson	p is constant over a large range of dilution
Mn^{++}	23	$MnCl_2$, $MnSO_4$, $Mn(NO_3)_2$	29·4	Piccard	p changes with time, otherwise it is fairly constant
Cr^{+++}	21	$Cr(NO_3)_3$, $Cr_2(SO_4)_3$	19·0 18·97	Weiss	Violet and green salts constitute a complex chemical problem but the moments are more or less constant, varying between 18·97 and 18·3; in the complex green sulphate when a drop of H_2SO_4 is added $p=19$
Cr^{++}	22	$CrSO_4$	23·8 (24)	Cabrera	Difficulties due to oxidation make the determination difficult

the formation of ions of the $(CoCl_3)'$ and $(CoCl_4)''$ type, and it is clear that the addition of Cl' to the $CoCl_2$ will have the effect of bringing down the value of p, as happens to be the case.

That the decrease of the Weiss magneton value for the cobalt salts in alcoholic and HCl solutions cannot be explained on the production of anhydrous or dihydrate $CoCl_2$ is further proved by the observation of Foëx[16] that the value of p for cobalt chloride in concentrated sulphuric acid (when it should be completely dehydrated) is 25·66 and not between 22 and 23, as is the case with the solutions investigated above.

What appears to be the most accurate work on the magnetic properties of cobalt chloride is that of Trümpler and Cabrera[17]. Trümpler with many solutions obtained a constant value of 24·5 for the Weiss magneton number. The values of Trümpler and Cabrera under all conditions of dilution varied between 24 and 24·6. Chatillon[18] showed that the above variation is due to the existence of an unstable salt. For aqueous solutions of $CoCl_2$, $CoSO_4$ and $Co(NO_3)_2$ Chatillon got a value of 25·25 for the Weiss magneton number.

Specimens of $CoCl_2$ from Cabrera's laboratory showed in aqueous solution at first a variation of p with concentration and a variation of Δ with temperature. After five months Chatillon noticed that all these irregularities disappeared and the value of p was 25·02 and that of $\Delta = -11°$ .Thus Chatillon shows that the only stable magnetic state for aqueous solutions of cobalt salts is one with a constant integral value of $p = 25$ and $\Delta = -11°$.

In amyl alcohol and ethyl alcohol cobalt chloride gave the value of 23 for p, and the aqueous solutions of $CoCl_2$ diluted with hydrochloric acid gave results depending on the concentration of the acid. It appears that similar solutions do not always give the same result; the temperature variation is linear only over a limited range and magneton numbers 22, 23, 24, 25 and 26 are found.

6. SOLID PARAMAGNETICS

Perhaps the largest amount of work on paramagnetism has been done on solid paramagnetics. The notable workers in this field are Honda and Owen[19] on elements, Honda and Ishiwara[20] on salts and oxides, and Foëx[21], Theodorides[22] and Jackson[23], all of whom have also worked on salts and have elucidated many interesting points. Over limited ranges of temperature the susceptibilities follow either the Curie or the Weiss law and a graph of $\frac{1}{\chi}$ against T gives a straight line.

Over higher ranges of temperature several irregularities show themselves in the curves representing the relation between the temperature and susceptibility, the more common of which are given below:

(i) The lines show a gradual curvature.

(ii) One or more than one abrupt changes follow in the general course of the line.

(iii) A jump occurs from one parallel line to another.

As mentioned before, theory requires a linear relation between χ and $\frac{1}{T}$. In the calculation of the values of the magnetic moments for solids (see below) only linear portions of the curves have been utilised.

A brief summary of the metallic salts investigated for the experimental determination of magnetic moment value is given below. The latter are given in terms of the Weiss magneton p.

Vanadium.—Only $VOSO_4.3\frac{1}{2}H_2O$ has been investigated between $-79°$ and 100° C. The value of the magnetic moment is found to be 8·95 units.

Chromium.—It has been investigated by Honda at different ranges of temperature and its magnetic moment has been found to have a value of 18·9 units.

Manganese.—For bivalent manganese salts, viz. $MnCl_2$, $MnSO_4$, $MnSO_4.4H_2O$, the value of magnetic moment has been found to be 28·45, 29·04 and 29·04 respectively. Slightly different results have been reported by Ishiwara, Weiss and Honda, who claim a value of 27·04 units for $MnCl_2$ between $-180°$ and 630° C.

Iron. — Ferrous salts like $FeCl_2$, $FeCl_2.4H_2O$, $FeSO_4$, $FeSO_4.7H_2O$, $Fe(NH_4)_2(SO_4)_2.6H_2O$, have value of magnetic moment varying between 25·9 for $FeCl_2$ and 26·08 for $FeSO_4$. In general, the values of the magnetic moment of ferrous salts are constant.

Ferric Salts.—Both the ferric salts examined, viz. $Fe_2(SO_4)_3$ and $Fe_2(SO_4)_3(NH_4)_2.SO_4$, have a magnetic moment equal to 29·0.

Cobalt.—The values of the magnetic moments for $CoCl_2$, $CoSO_4$, $CoSO_4.7H_2O$ and $Co(NH_4)_2(SO_4)_2.6H_2O$ are 24·96, 25·0, 25·04 and 24·75 respectively. Only anhydrous $CoSO_4$ shows a value of 26·0.

Nickel.—Nickel chloride has been investigated by various workers, and the value arrived at lies between 16·03 and 16·92.

$NiSO_4$, on the other hand, shows a uniform value of 17·0 approximately as investigated by Jackson and Theodorides.

Copper.—The values of the magnetic moments of copper chloride and sulphate are respectively 9·2 and 9·6, in fair agreement with one another.

A table of the magnetic moments of the rare earth salts is given below.

TABLE II

WEISS MAGNETON NUMBERS OF RARE EARTH SALTS

Ion^{+++}	Number of Electrons in the Ion	Salt Investigated	Weiss Magneton Number p *
La	54	$La_2(SO_4)_3 . 8H_2O$	0·0
Ce	55	$Ce_2(SO_4)_3 . 5H_2O$	11·89
Pr	56	$Pr_2(SO_4)_3 . 8H_2O$	17·89
Nd	57	Nd_2O_3	18·05
Sm	59	$Sm_2(SO_4)_3 . 8H_2O$	7·77
Eu	60	$Eu_2(SO_4)_3 . 8H_2O$	17·92
Gd	61	$Gd_2(SO_4)_3 . 8H_2O$	40·07
Tb	62	$Tb_2(SO_4)_3 . 8H_2O$	47·92
Ds	63	$Ds_2(SO_4)_3 . 8H_2O$	52·55
		Ds_2O_3	52·00
Ho	64	$Ho_2(SO_4)_3 . 8H_2O$	52·00
Er	65	$Er_2(SO_4)_3 . 8H_2O$	46·98
		Er_2O_3	47·09
Tu	66	$Tu_2(SO_4)_3 . 8H_2O$	35·85
Yb	67	$Yb_2(SO_4)_3 . 8H_2O$	21·74
Cp	68	$Cp_2(SO_4)_3 . 8H_2O$	0·0

* Mean values from International Critical Tables.

A close perusal of Table II in conjunction with the data on solutions (Cf. Table IV, Decker) reveals, amongst other points, the striking fact that the values of magnetic moments both in solution and the solid state are the same for the same active ion. A regular step-by-step variation in the magneton number for ions of rare earth metals, especially the regular increase from a minimum to a maximum in passing from Samarium to Dysprosium and back to zero again in the case of Lutecium, is rather an important fact which has been considered later both on the classical as well as the modern theories.

The study of the paramagnetic properties of the elements has been especially very useful. A complete list of the elements whose susceptibility decreases with temperature has already been given in Chapter IV. Of these there are many elements whose susceptibility does not decrease linearly with temperature but shows a slight inflexion towards the temperature axis. Stoner in his excellent book *Magnetism and Atomic Structure* suggests that their susceptibility may be given by

$$\chi=\frac{C}{T-\Delta}-\chi_d$$

where χ_d is an underlying diamagnetic susceptibility. This value has been determined in many cases.

7. ANOMALOUS PARAMAGNETISM

In spite of the universality of the behaviour of paramagnetics in showing a decrease in the susceptibility with temperature, exceptions are on record where the susceptibility either shows an increase with temperature or remains constant. Of particular importance are salts like $KMnO_4$, $K_2Cr_2O_7$, $KCrO_4$, $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. Paramagnetism in these salts is small and is as a rule independent of temperature. As a matter of fact $K_4Fe(CN)_6$ is diamagnetic, but when correction is made for the diamagnetism of K and CN it shows a slight residual paramagnetism for the atom of Fe($\chi_M=29{\cdot}8\times10^{-6}$). Similarly the value of χ_M for Mn in $KMnO_4$ is equal to $64{\cdot}4\times10^{-6}$.

Independence of paramagnetic susceptibility with temperature is exhibited by many elements, a complete list of which has been given in the chapter on Pan-magnetism.

In spite of its being the subject of many investigations, no satisfactory explanation of the phenomenon has yet been put forward, although an attempt has been made to explain it in the case of alkali metals by W. Pauli (junior) and Bloch on the concept of free electrons (cf. Section 15). The subject has also been recently discussed by Van Vleck, who shows that a term for 'residual paramagnetism independent of temperature' is unavoidable when susceptibilities are calculated for molecules of ions containing many atoms.

8. SULPHIDES AND OXIDES

Although the sulphides and oxides have not been examined over a large range of temperatures the results seem to warrant further research. The case of the sulphides of vanadium V_2S_5, V_2S_3 and VS is of special interest when examined side by side with the oxides V_2O_5, V_2O_3 and VO. The gram-molecular susceptibility χ_M for these compounds is shown in the following table:

TABLE III

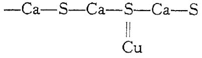
Substance	$\chi_M \times 10^6$
V_2S_5	1645
V_2O_5	77
V_2S_3	886
V_2O_3	1040
VS	600
VO	3350

It is apparent that while the χ_M values for oxides increase in the order $V_2O_5 < V_2O_3 < VO$, the corresponding values of sulphides run in the reverse order: $V_2S_5 > V_2S_3 > VS$.

9. LUMINESCENT SULPHIDES

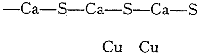
A further impetus to the study of sulphides has been given by the important contributions of E. Rupp [24] on the magnetic behaviour of phosphorescent sulphides. From their mode of preparation, which consists in combining atoms of an alkaline earth, say calcium, with sulphur and the atom of a heavy metal, Lenard and Klatt [25] have postulated the mechanism of phosphorescence in terms of the structure of such molecular arrangements.

According to Lenard [26] a phosphorescent centre consists of a combination of a large number of molecules of an alkaline earth sulphide in a ring-like formation within which the atom of the heavy metal is attached to one of the sulphur atoms. Thus a $CaCu_\alpha$ centre of phosphorescence which emits red bands (α bands of Lenard) on excitation can be represented by the formula



$$\text{—Ca—S—Ca—}\underset{\underset{\text{Cu}}{\|}}{\text{S}}\text{—Ca—S}$$

In order to explain the possibility of the metallic atoms producing different colours of phosphorescent bands the values of the valency of this atom are supposed to be capable of variation. Thus a $CaCu_\beta$ centre which emits blue bands may have the structure



$$\begin{array}{c}\text{—Ca—S—Ca—S—Ca—S}\\ \\ \text{Cu}\quad\text{Cu}\end{array}$$

Tomaschek[27] has examined a large number of phosphorescent substances containing rare earths and has suggested the alternative view that a heavy metallic atom is not immediately connected to a sulphur atom in a molecular group, but that the sulphide of the metallic atom is attached to an atom of the alkaline earth and that the different phosphorescent bands may be explained on the properties of the various sulphide combinations of the atoms of the heavy metal present. This question could be settled once for all if we could analyse the fluorescent centres chemically, but as this is not possible indirect information on this structure is the only alternative left, and for this the various physical properties of the luminescent sulphides have to be investigated. Magnetically speaking these phosphorescent sulphides generally consist of a diamagnetic material like CaS (together with some diamagnetic fluxes like NaCl) in which paramagnetic atoms such as Mn or diamagnetic atoms like Cu are embedded. Rupp has taken into consideration the magnetic behaviour of these substances and has attempted to correlate the magnetic susceptibility and other factors such as the formation of complex molecular groups, their distortion under pressure, the nature of radiations emitted by the same constituents and the influence of temperature. A study of this paper in original is recommended to all those interested in the subject. We shall only consider here some of the important results obtained by Rupp and take them one by one.

(i) He showed that groups of molecules of the basic materials —Ca—S and —Ca—O are more paramagnetic than the simple CaS or CaO.

(ii) Even the luminescent substances containing ZnS are more paramagnetic when they exhibit phosphorescence than when they are non-excited.

(iii) In the case of phosphorescent materials like CaMn, ZnMn, substances which contain very small traces of Mn, the susceptibility measurements indicate the presence of MnS.

(iv) The presence of MnS is confirmed by the nature of absorption bands whose edges correspond to divalent S combinations of Mn.

(v) When diamagnetic metals like Bi, Cu and Ag are added in small quantities in the production of the luminescent sulphides their susceptibilities become about 1000 times more than their normal mass susceptibility. This increase in diamagnetism is attributed by Rupp to the isolation of the atoms of the metals. The increase in diamagnetism is greatest in the case of Bi and then follow Ag and Cu in order.

Although the increased diamagnetism in case of Bi, Cu, Ag makes it difficult to decide definitely, it appears probable that the nature of chemical combination as in the case of Mn suggests a sulphide formation. In fact a Ca-Cu combination with a fairly high copper content gave an atomic susceptibility for copper which indicated a value between that of CuS and Cu_2S. The magnetic behaviour of phosphorescent substances containing metals of the rare earths is extremely important because these rare earths possess enormously large atomic susceptibilities, their oxides possess even larger susceptibilities and the phosphorescence of these substances is characterised by the emission of sharp spectral lines[27].

In phosphorescent materials containing CaS, SrS, BaS, SrO, CaO as basic substances with Sm as the metallic constituent it has been noticed that the values of their susceptibilities are as a rule considerably lower than for luminescent materials containing an equal amount of Mn. There seems also to exist a relationship between the width of the doublets and the sharpness of the lines emitted by the luminescent materials and the decrease in paramagnetism corresponding to a decrease in the amount of Sm in the body. Thus the magnetic data bring into prominence the view that in the luminescent centres there must exist electron orbits which circumscribe the whole phosphorescent centre and that it is these orbits which are responsible for the emission of light perhaps as the outer orbits of an electron liberated from the metal which gets excited.

10. PARAMAGNETISM AND ADSORPTION

That the adsorption of paramagnetic ions is capable of yielding useful information regarding the mechanism of sorption has been shown by Bhatnagar, K. N. Mathur and Kapur[28]. They investigated the adsorption of salts of Fe, Ni, Co and Mn by various types of charcoal and silica. In the case of the charcoals they showed that all the paramagnetic ions adsorbed exhibited diamagnetism. Cocoanut charcoal which itself was feebly paramagnetic became markedly diamagnetic after adsorbing the paramagnetic ions. Animal and almond charcoals which were initially paramagnetic owing to paramagnetic impurities of inorganic origin became less paramagnetic after adsorption contrary to the usual mixture law. From these results it would appear that adsorption is a phenomenon not analogous to simple mixing and that much more profound changes take place between the adsorbent and the adsorbed materials in the process of adsorption, making it almost analogous to a quasi-chemical or chemical action.

The specificity of this behaviour is brought out into prominence by the fact that in the case of adsorption by silicic acid or silica there was a slight increase of paramagnetism. These facts are capable of being explained on the assumption that complexes are formed during the process of adsorption. When the ions of the transition group form complexes with groups containing carbon, such as CN and CO as in ferrocyanides and iron carbonyls, the complexes exhibit diamagnetism, while with silica the compounds and complexes are paramagnetic.

In this connection it would be interesting to refer to a paper by Biggs[29] on the decrease of paramagnetism of palladium which had absorbed (or more accurately adsorbed) hydrogen. Biggs concludes that after correcting for the known diamagnetism of hydrogen there still remains a large decrease in the susceptibility. This, he observed, is probably due to some interaction of the hydrogen and palladium whereby the latter's paramagnetism is reduced.

11. LANGEVIN'S EQUATION ON QUANTUM THEORY

Many attractive possibilities have been opened in the subject of paramagnetism as a result of the development of quantum mechanics. The theory of spectra as developed by Hund[30] and the interpretation of para- and diamagnetism on quantum mechanics by Van Vleck have been applied with remarkable success to the explanation of the baffling phenomenon of paramagnetism—the rare earth ions and the paramagnetic gases—which had resisted the classical theories for close upon quarter of a century.

In deriving Langevin's equation (Section 1) the probability of distribution of molecular magnetic axes was taken proportional to $e^{a \cos \alpha}$. When $a \left(=\frac{\mu H}{kT}\right)$ is small, $e^{a \cos \alpha}$ is approximately equal to $1+a\cos\alpha$ and the equations (4) and (5) for $\bar{\mu}$ and μ could be written as

$$\frac{\bar{\mu}}{\mu}=\frac{a\int_0^\pi \cos^2\alpha\sin\alpha d\alpha}{\int_0^\pi \sin\alpha d\alpha}$$

$$=a\,\overline{\cos^2\alpha} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

the bar indicating a spatial mean square value. On classical statistical mechanics the angle α which the magnetic axes make with the field direction can assume continuous values from 0 to π and consequently the integrated value of $\overline{\cos^2\alpha}$ comes to $1/3$, leading to the Langevin relation

$$\frac{\bar{\mu}}{\mu}=\frac{a}{3}$$

On the quantum theory, however, this assumption is no longer justified, as the atom could only assume certain discrete orientations in the presence of the field.

For an atom with Russell-Saunders coupling and characterised by the quantum numbers L, S, M it was shown in Chapter V, equation (12), that in the presence of a magnetic field the energy of precession has the value

$$W_m=Mg\frac{eh}{4\pi m_0 c}\mathrm{H}$$

where the magnetic quantum number M can take $(2J+1)$ values, J, $J-1$ . . . 0, . . . $-J+1$, $-J$.

In accordance with the Boltzmann distribution law the states with low field energy will be favoured over those with high energy, so that the average field energy is given by

$$\overline{W}=\frac{\sum\limits_{M=-J}^{M=+J} W_m e^{-\frac{W_m}{k\mathrm{T}}}}{\sum\limits_{M=-J}^{M=+J} e^{-\frac{W_m}{k\mathrm{T}}}} \quad . \quad . \quad . \quad (25)$$

which on expanding the exponential and substituting the values gives

$$\overline{W}=-\left(\frac{eh}{4\pi m_0 c}\right)^2\mathrm{H}^2 g^2\frac{J(J+1)}{3k\mathrm{T}} \quad . \quad . \quad (26)$$

or writing $\mu_J H = \overline{W}$

$$\mu_J \frac{H}{3kT} J(J+1) g^2 \left(\frac{eh}{4\pi m_0 c}\right)^2 \quad . \quad . \quad (27)$$

Comparing this with equation (10) of this chapter, viz.

$$\bar{\mu} = \frac{\mu}{3kT} H$$

we have

$$\mu^2 = J(J+1) g^2 \left(\frac{eh}{4\pi m_0 c}\right)^2 \quad . \quad . \quad . \quad (28)$$

which gives for the molecular magnetic moment the value

$$\mu = g\sqrt{J(J+1)} \frac{eh}{4\pi m_0 c}$$

$$= g\sqrt{J(J+1)} \text{ in Bohr magneton units} \quad . \quad (29)$$

in which g, the Lande splitting factor, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \text{ (cf. Chapter V, Section 16).}$$

The equation (29) thus connects the measurements of paramagnetic susceptibilities with the spectroscopic spectral states or the Zeeman term separations of the atom.

In the simplest case, that of atoms in the S state for which the orbital moment $L=0$, the magnetic moment is entirely due to the electron spins, so that $J=S$ and $g=2$ (from Chapter V, Table III). This gives

$$\mu_S = 2\sqrt{S(S+1)} \text{ or } \sqrt{4S(S+1)} \text{ in Bohr units} \quad (30)$$

In terms of the Weiss magneton number p, this may be written as

$$p = 4{\cdot}952\sqrt{4S(S+1)} \quad . \quad . \quad . \quad (31)$$

For atoms in the singlet S state the orbital and spin moments are both zero and this gives for the resultant magnetic moment the value zero. The atom in this state is consequently diamagnetic.

For the doublet ^2S state the spin moment $S=1/2$ and equation (30) gives $\mu_S=\sqrt{3}$, so that for atoms in this state the magnetic moment calculated from susceptibility measurements should be $\sqrt{3}$ Bohr magneton or $p=8{\cdot}58$.

12. VAN VLECK'S GENERAL THEORY OF PARAMAGNETISM

In the previous section the Langevin formula has been derived applying the quantum principles to a particular atomic model. Van Vleck[31] has given a more general derivation of the Langevin-Debye formula based on the new quantum mechanics and making only the fundamental assumption that the momenta matrix involves only elements whose frequencies are either small or large compared to $\frac{kT}{h}$. Van Vleck's derivation gives for magnetic susceptibility

$$\chi = \frac{N\overline{\overline{\mu^2}}}{3kT} + N\bar{\bar{\alpha}} \quad . \quad . \quad . \quad . \qquad (32)$$

where $\overline{\overline{\mu^2}}$ is written for $\sum_{j,m} \mu^2(j;j)e^{-\frac{W_{nj}}{kT}} \Big/ \sum_{j,m} e^{-\frac{W_{nj}}{kT}}$ and denotes the statistical mean square of the moment μ, i.e. the time average $\mu^2(j;j)$ of the square (μ^2) of the low-frequency part of the magnetic moment vector, this average itself being averaged over the various component levels of the normal state weighted in accordance with the Boltzmann factor $e^{-\frac{W_{nj}}{kT}}$. The term $N\bar{\bar{\alpha}}$ is given by

$$N\bar{\bar{\alpha}} = \tfrac{2}{3}N \sum_{n' \neq n} \frac{|m^\circ(n;n')|^2}{h\nu(n';n)} - \frac{Ne^2}{6mc^2}\Sigma\overline{r^2} \qquad (33)$$

This is seen to be the joint contribution of (i) the high-frequency elements of the paramagnetic moment, and (ii) the diamagnetic effect.

Van Vleck's complete equation

$$\chi_M = \frac{N\overline{\overline{\mu^2}}}{3kT} + \tfrac{2}{3}N \sum_{n' \neq n} \frac{|m^\circ(n;n')|^2}{h\nu(n';n)} - \frac{Ne^2}{6mc^2}\Sigma\overline{r^2} \quad . \qquad (34)$$

therefore includes three terms:

(*a*) $\frac{N\overline{\overline{\mu^2}}}{3kT}$, the contribution of the low-frequency matrix elements to paramagnetism, is identical with the Langevin formula derived before and is seen to be dependent on temperature.

(*b*) $\frac{2}{3}N\Sigma \frac{m^\circ(n;n')}{h\nu(n';n)}$, the contribution of the high-frequency elements to paramagnetism, is independent of temperature, and (*c*) $-\frac{Ne^2}{6mc^2}\Sigma\overline{r^2}$, the underlying diamagnetism, is also independent of temperature.

Van Vleck's treatment of paramagnetism refers only to atoms with Russell-Saunders coupling, i.e. where the spin angular momenta s of all the electrons can combine to form a resultant S, and independently the orbital angular momenta l combine to form a resultant L (cf. Chapter V, Section 11). According to Chapter V, Section 16, the magnetic moment of an atom consists of two components, viz. the 'orbital' and 'spin' parts, and these two may be inclined to each other at different angles. This will be the case if the normal state contains a spin multiplet whose term separation $\Delta\nu$ corresponding to values of $J=L-S \ldots L+S$ (with the same L and different values of S) are small compared to kT. Because of this variation in the angle between L and S the resultant magnetic moment cannot be regarded the same for all normal states. The result of this is that in Van Vleck's equation (32) the part $N\bar{\bar{\alpha}}$ has to be retained, which otherwise on the hypothesis of a 'permanent' magnetic moment would be zero.

We now consider separately two limiting cases in which the spin multiplets are (i) very narrow and (ii) very wide compared to kT. These two cases are important as the derivation of equation (32) was based upon them as assumptions.

(i) *Spin Multiplet Interval small compared to k*T.—In the absence of a magnetic field the resultant angular momentum $\mathbf{J}$ given by $\mathbf{L}+\mathbf{S}$ will be constant both in magnitude and direction. The magnetic vector is given by $\mathbf{L}+2\mathbf{S}$ (since the spin magnetic moment is twice the spin mechanical moment), and it follows from considerations of vector directions that $\mathbf{L}+2\mathbf{S}$ or the perpendicular component of S on J (b–c in the figure) will not remain constant in direction due to the continual precession of L and S about J. Now according to Van Vleck the only periodic elements involved in the magnetic moment vector

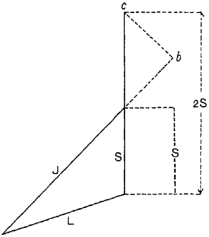


FIG. 34.

$\boldsymbol{m}=-\beta(\mathbf{L}+2\mathbf{S})$ of an atom are those associated with the precessions of the $\mathbf{S}$ and $\mathbf{L}$ vectors about $\mathbf{J}$. Thus when the spin multiplet intervals $\Delta\nu$ are small compared to kT (i.e. when the precession of L and S about J is slow) these periodic elements are entirely of the low-frequency type, consequently for this limiting condition the high-frequency elements should all vanish. Such a high-frequency element is contained in the first term of the right-hand member of equation (33). If, further, the diamagnetic contribution is also small, then the entire expression (33) becomes negligible and the susceptibility is given by the equation (32) without $\mathrm{N}\bar{\bar{\alpha}}$.

In the absence of high-frequency elements, however, μ becomes identical with the magnetic vector, $-\beta(\mathbf{L}+2\mathbf{S})$, so that

$$\overline{\overline{\mu^2}}=(4\mathbf{S}^2+\mathbf{L}^2+4\overline{\overline{\mathbf{LS}}})\beta^2 \quad . \quad . \quad . \quad (35)$$

For large fields $\overline{\overline{\mathbf{L}.\mathbf{S}}}$ may be taken to be zero, since the interaction between $\mathbf{S}$ and $\mathbf{L}$ will be small in this case and they will be quantised separately relative to the field (cf. Chapter V, Section 17). Further, it could be shown that the statistical average of $\mathbf{L}.\mathbf{S}$ vanishes also in weak fields. Hence replacing S^2 by $S(S+1)$ and L^2 by $L(L+1)$, we get

$$\overline{\overline{\mu^2}}=[4S(S+1)+L(L+1)]\beta^2 \quad . \quad . \quad (36)$$

and the susceptibility equation for $\Delta\nu\rightarrow 0$ or $\mathrm{T}\rightarrow\alpha$ becomes

$$\chi_{\mathrm{M}}=\frac{\mathrm{N}\beta^2}{3k\mathrm{T}}[4S(S+1)+L(L+1)] \quad . \quad . \quad (37)$$

where β is the Bohr magneton.

(ii) *Multiplet Intervals large compared to k*T.—In this condition the normal state is given by the one component which has the lowest energy. The double bar over μ^2 is therefore no longer needed. The matrix elements of the magnetic vector are now all of the high-frequency type except for $\Delta J=0$.

Van Vleck has shown in this case that

$$\mu^2=\beta^2\left[\frac{\mathbf{L}.\mathbf{J}}{|\mathbf{J}|}+2\frac{\mathbf{S}.\mathbf{J}}{\mathbf{J}}\right]^2 \quad . \quad . \quad . \quad (38)$$

which reduces to

$$\mu^2=g^2\beta^2J(J+1) \quad . \quad . \quad . \quad (39)$$

where g is the Lande splitting factor given by

$$g=1+\frac{S(S+1)+J(J+1)-L(L+1)}{2J(J+1)}$$

The complete equation for susceptibility now becomes

$$\chi_{M}=\frac{Ng^{2}\beta^{2}J(J+1)}{3kT}+N\alpha \quad . \quad . \quad . \quad (40)$$

The value for Nα, neglecting the diamagnetic part, is given by Van Vleck from consideration of the second order Zeeman term. This part arises from the component of $\boldsymbol{m}$ perpendicular to **J** (i.e. *b–c* of Fig. 34), which in this case contributes only to the susceptibility part independent of temperature rather than the ordinary Curie part as in the previous case. Van Vleck gives for Nα the value

$$N\alpha=\frac{N\beta^{2}}{6(2J+1)}\left[\frac{F(J+1)}{2h\nu(J+1;J)}-\frac{F(J)}{h\nu(J;J-1)}\right] \quad . \quad (41)$$

with the abbreviation

$$F(J)=\frac{1}{J}[(S+L+1)^{2}-J^{2}][J-(S-L)^{2}]$$

In the more usual case where the normal state is $J_{\max}$ or $J_{\min}$ depending on whether the multiplet is inverted or regular the first or the second part of equation (41) vanishes.

(iii) *Multiplet Intervals comparable to k*T.—The intermediate case in which the multiplet intervals $\Delta\nu$ are comparable to kT may also be discussed. In this case the effect of the inner quantum number J is comparable with kT. The derivation is based on the idea that the total number of atoms N is made up of groups of atoms N_J with different J values, thus giving $N=N_{J_1}+N_{J_2}+N_{J_3}$ . . ., etc. The contribution to susceptibility by each of the N_J groups will be given by equation (40) with N replaced by N_J. The number of atoms in any group N_J will be determined by the Boltzmann temperature factor and is thus proportional to $(2J+1)e^{-\frac{W_J}{kT}}$, since for a given J there are $(2J+1)$ component states with different magnetic quantum numbers. Thus Van Vleck [32] gives

$$\chi_{M}=\frac{N\sum\limits_{J=|L-S|}^{L+S}\{[g^{2}_{J}\beta^{2}J(J+1)/3kT]+\alpha_{J}\}(2J+1)e^{-\frac{W_J}{kT}}}{\Sigma(2J+1)e^{-\frac{W_J}{kT}}} \quad (42)$$

where the subscripts on g and α denote that they are explicit functions of J. In the limiting case of very narrow multiplets the equation reduces to (37).

13. PARAMAGNETISM OF THE RARE EARTHS AND THE IRON GROUP

In considering the applications of the theoretical equations we come across the difficulty of obtaining paramagnetic substances in the gaseous or vapour state for which alone the theory should hold with accuracy. In the somewhat similar condition of dilute solutions another difficulty is encountered. The paramagnetic property arises from the presence of outer valence electrons in the atom, but in solution these electrons are stripped to form ions, leaving behind closed atom-cores which are diamagnetic. For example, both K and Cl atoms contain an odd number of valence electrons and are paramagnetic, but in a solution of KCl the ion K^+ loses an electron and Cl^- captures an electron, each assuming the closed argon configuration. Consequently the solution of KCl behaves as diamagnetic. Also, polar salts like KCl are known to be ionised even in the solid state and are diamagnetic for the same reasons.

Elements of the transition series and the rare earths form an exception to this. All these elements, besides containing the outer valence electrons, contain an incomplete inner group. This has been discussed before in Chapter V, Section 23, and will be clear from the table of elements given there. For iron group the incomplete inner shell is $3d$, for palladium group $4d$, for rare earths $4f$ and for the platinum group $5d$. The rare earth salts are trivalent and are ionised both in solid salts and in solution. They lose, in consequence, the outer $5d$ and $6s$ electrons. The paramagnetism of rare earth ions is, then, due to the incomplete $4f$ sub-shell. This brings us to an important difference between the rare earths and the transitional groups. In the rare earth ions the paramagnetic $4f$ sub-shell is embedded in the outer shells of two $5s$ and six $5p$ electrons characteristic of inert gas configuration and of higher principal quantum number; on the other hand, in the ions of the iron and other transitional groups, as the valence electrons are removed, the incompleted sub-shell lies outermost. Hence it is easy to understand the suggestion that in them the solvent molecules or the surrounding atoms or ions interact sufficiently to disturb the orbital magnetic moment completely or partially and leave only the spin moment to account for their magnetic behaviour.

It is not surprising, therefore, that the rare earth ions and the iron group ions require different treatment.

(*a*) *The Rare Earth Ions.*—Hund [33] first calculated the susceptibilities of the rare earth ions under the assumption that the multiplet intervals are wide compared to kT. The moments were calculated by him according to equation (29), neglecting the second order Zeeman term $N\alpha$ as given in the more complete equation (40).

The results of Hund's calculations are given in Table IV. These results are expressed in terms of the effective Bohr magneton number

$$\mu_B = \sqrt{\frac{3\chi_M kT}{N\beta^2}} = 2{\cdot}839\sqrt{\chi_M T}^* \quad . \quad . \quad (43)$$

The calculation of normal spectroscopic states was made by Hund on the basis of his spectroscopic theory using the Pauli exclusion principle. In Table IV the normal term values are also given. These values have found reliable confirmation on both magnetic as well as spectroscopic data.

Van Vleck and Miss Frank [34] have calculated the susceptibilities of rare earth ions using the complete equation (40) for susceptibility

$$\chi_M = \frac{N\beta^2}{3kT} g^2 J(J+1) + N\alpha$$

The effect of the inclusion of $N\alpha$ which arises from the second-order Zeeman terms removes the glaring discrepancy between theoretical and experimental values for Sm^{+++} and Eu^{+++}, which were the weak points of Hund's theory for rare earths. The inclusion of the second-order Zeeman correction has also explained the temperature anomaly [35] for Sm and Eu.

(*b*) *The Iron Group.*—The salts of the iron group have been treated by Sommerfeld and Laporte [36] by taking the limiting cases where $\Delta\nu = 0$ and $\Delta\nu = \infty$, i.e. corresponding to equations (37) and (40). In an important paper Laporte [37] also made accurate calculations corresponding to the actual $\Delta\nu$ separations, which were intermediate between the two limiting values.

It has been noted by Sommerfeld [38], Bose [39], Stoner [40] and others that the susceptibilities of the iron group ions are given to a high degree of accuracy according to the formula

$$\chi_M = \frac{N\beta^2}{3kT}[4S(S+1)]$$

which neglects the orbital moment completely. The iron group salts, as also their complex molecules, have been further discussed in Chapter IX, Sections 12-18.

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* It should be pointed out that defined in this way μ_B is a function of temperature unless Curie's law $\chi_M T = \text{const.}$ is obeyed.

TABLE IV

THEORETICAL AND EXPERIMENTAL MAGNETIC MOMENTS FOR RARE EARTH IONS

Incomplete Sub-shell	Ion and Normal Term	Theoretical μ_B		Experimental μ_B			
		Hund	Van Vleck and Frank	Cabrera (Sulphate)	Meyer (Sulphate)	Decker (Solution)	Cabrera and Duperier
	La^{+++} $^{1}S_{0}$	0·00	0·00	..	..	..	..
$4f$	Ce^{+++} $^{2}F_{5/2}$	2·54	2·56	2·39	2·77	2·10	..
$4f^2$	Pr^{+++} $^{3}H_{4}$	3·58	3·62	3·60	3·47	3·41	3·47
$4f^3$	Nd^{+++} $^{4}I_{9/2}$	3·62	3·68	3·62	3·51	3·45	3·52
$4f^4$	Ill^{+++} $^{5}I_{4}$	2·68	2·83	..	..	..	..
$4f^5$	Sm^{+++} $^{6}H_{5/2}$	0·84	1·55 1·65	1·54	1·51*	1·63	1·58
$4f^6$	Eu^{+++} $^{7}F_{0}$	0·00	3·40 3·51	3·61	3·12	..	3·54
$4f^7$	Gd^{+++} $^{8}S_{7/2}$	7·94	7·94	8·2	8·1	7·86	7·9
$4f^8$	Tb^{+++} $^{7}F_{6}$	9·72	9·7	9·6	9·0	9·8	9·6
$4f^9$	Ds^{+++} $^{6}H_{15/2}$	10·65	10·6	10·5	10·6	10·9	10·3
$4f^{10}$	Ho^{+++} $^{5}I_{8}$	10·61	10·6	10·5	10·4	10·4	10·4
$4f^{11}$	Er^{+++} $^{4}I_{15/2}$	9·58	9·6	9·5	9·4	9·5	9·4
$4f^{12}$	Tu^{+++} $^{3}H_{6}$	7·56	7·6	7·2	7·5	..	7·0
$4f^{13}$	Yb^{+++} $^{2}F_{7/2}$	4·54	4·5	4·4	4·6	4·5	4·3
$4f^{14}$	Cp^{+++} $^{1}S_{0}$	0·00	0·0	..	0·0	1·2 (?)	..

* Corrected for diamagnetism by Zernicke and James.

NOTE.—In the table the theoretical values of Van Vleck and Frank differ from Hund in the extra term $N\alpha$ for susceptibility. These values are a function of temperature, except the term $N\alpha$ in Van Vleck's values. This is important only for Sm and Eu. Experimental values are given from the data of Cabrera (*Compt. rend.* **180**, 668, 1925) for sulphate octahydrate, who employed the preparations of Urbain (*Compt. rend.* **147**, 1286, 1908; **149**, 37, 1909; **159**, 323, 1924) and of Auer von Welsbach; Stefan Meyer (*Phys. Zeits.* **26**, 51, 478, 1925) for sulphate $8H_2O$, who employed the materials of Auer von Welsbach; Decker (*Ann. der Physik*, **79**, 324, 1926) also used Welsbach's preparations but determined susceptibilities of sulphates in aqueous solutions except for Ce, Pr and Nd for which nitrates were used from Prandtl. Zernicke and James (*J. Amer. Chem. Soc.* **48**, 2827, 1926) gave details of the preparation and purification of their salts. Sulphate crystals with $8H_2O$ were employed, except for Ce which had $5H_2O$. Corrections were made for the diamagnetism of the (SO_4) ion from Pascal's value $-33{\cdot}9\times10^{-6}$ and of water $(-0{\cdot}72\times10^{-6})$. Cabrera and Duperier's (*Compt. rend.* **188**, 1640, 1929) measurements are on anhydrous sulphates from Auer von Welsbach. The magneton numbers for Cabrera and Stefan Meyer are taken from International Critical Tables and for Cabrera and Duperier from Van Vleck's calculations. It has not been possible to include here the experimental values of Du Bois (*Ber.* **33**, 3344, 1899) solutions, Urbain, Wedekind (*Ber.* **54**, 253, 1921) and E. H. Williams (*Phys. Rev.* **12**, 158, 1918; **14**, 348, 1919) oxides.

14. THE PARAMAGNETIC SUSCEPTIBILITIES OF OXYGEN AND NITRIC OXIDE

Oxygen and nitric oxide constitute the two best-known examples of paramagnetism in the gaseous state. All molecules containing an odd number of electrons are as a rule paramagnetic. The case of oxygen is therefore of peculiar interest and has been responsible for much speculative work because this gas contains an even number of electrons and is still paramagnetic. In order to explain this anomaly G. N. Lewis[41] assumes that there is no double bond in the O_2 molecules. On the other hand the two electrons which are supposed to constitute the second bond are actually separate so that each atom has an odd electron and the electronic formula is $:\overset{..}{\underset{.}{O}}:\overset{..}{\underset{.}{O}}:$. G. N. Lewis emphasises the fact that the chemical characteristics of oxygen, its appreciable colour and reactivity strongly suggest that this gas is to be regarded as a molecule with odd electrons. An examination of the magnetic susceptibility of oxygen at various temperatures reveals the fact that the Curie law fails entirely when we compare oxygen at different temperatures and especially gaseous oxygen at room temperature with liquid oxygen.

The susceptibility of oxygen in the liquid and the solid state determined by Perrier and Onnes[42] shows that between 60° and 80° absolute the susceptibility of oxygen mixed with feebly diamagnetic nitrogen is given by

$$\chi=\frac{0\cdot315}{T-\Delta}$$

There are spurious effects observed at different concentrations and at different temperatures. At 33° absolute a new allotropic modification seems to be formed as the susceptibility decreases with decreasing temperature up to 13° abs.

Further, Perrier and Kamerlingh Onnes[42] show that if liquid oxygen is mixed with liquid nitrogen only at infinite dilution does it reach a value which corresponds with that which would be calculated by the Curie law from the susceptibility of oxygen at room temperature. The Leiden workers gave an explanation of this behaviour of oxygen on the view that the magnetic field of one molecule influences other neighbouring molecules, and this influence becomes negligible only at infinite dilution. They also hinted at the possibility of some sort of polymerisation being responsible for this behaviour. G. N. Lewis has developed the polymerisation theory and has shown that the magnetic properties of oxygen can be explained on the view that this gas is a mixture of O_2 and O_4, that the paramagnetism is due to O_2 and not to O_4, and that the unassociated O_2 portion of the gas obeys the Curie law.

There is a certain amount of uncertainty about the exact value of χ_M for oxygen. The most accurate values are shown in the following table.

TABLE V

EXPERIMENTAL SUSCEPTIBILITIES FOR OXYGEN

Gram-molecular Susceptibility	Name of Investigator
$3{\cdot}45\times10^{-3}$	Bauer and Piccard [43]
$3{\cdot}35\times10^{-3}$	Curie [44] (recalculated with $\chi=-0{\cdot}72\times10^{-6}$ for water)
$3{\cdot}31\times10^{-3}$	Onnes and Oosterhuis [45]
$3{\cdot}33\times10^{-3}$	Soné [46]
$3{\cdot}48\times10^{-3}$	Wills and Hector [47]
$3{\cdot}34\times10^{-3}$	Lehrer [48]
$3{\cdot}42\times10^{-3}$	Woltjer, Coppoolse and Wiersma [49]

Oxygen molecule has been given a normal state of the type $^3\Sigma$ both from its magnetic behaviour and an analysis of its band spectra by Mulliken.[50] Molecular Σ states are distinguished by an almost entire absence of multiplet structure, and hence in the case of oxygen it is possible to apply Van Vleck's equation (37) for multiplet separation $\ll kT$.

$$\chi_M=\frac{N\beta^2}{3kT}[4S(S+1)+L(L+1)]$$

For diatomic molecules having axial rather than central symmetry due to the two attracting nuclear centres the equation becomes

$$\chi_M=\frac{N\beta^2}{3kT}[4S(S+1)+\Lambda^2] \quad . \quad . \quad . \quad (44)$$

where Λ^2 replaces $L(L+1)$ for molecular $\Delta\nu\ll kT$.

In oxygen, according to the evidence of band spectra $S=1$ and $\Lambda^2=0$, and consequently we have

$$\chi_M=\frac{8N\beta^2}{3kT}=\frac{0{\cdot}993}{T} \quad . \quad . \quad . \quad (45)$$

where N is the Avogadro's number $=6{\cdot}06\times10^{23}$ and $\beta=0{\cdot}917\times10^{-20}$.

Formula (45) gives for the effective magnetic moment $\mu_B=2{\cdot}83$, and for the susceptibility of oxygen at 20° C. $\chi_M=3{\cdot}39\times10^{-3}$, which is in very good agreement with experimental values.

The susceptibility of the nitric oxide gas has been most accurately determined by Bauer and Piccard[43] and by Soné.[51] The results obtained by them are expressed in the following table.

TABLE VI

MAGNETIC DATA FOR NITRIC OXIDE

Mass Susceptibility at 20° C. $\chi \times 10^6$	Volume Susceptibility at 20° C. 760 mm. $\kappa \times 10^6$	χT	Susceptibility per Gram Molecule χ_M	Weiss Magneton p	Bohr Magneton μ_B
NO 48·7	0·0607	0·0143	$1{\cdot}46 \times 10^{-3}$	9·2	1·86

This gas has furnished the most striking confirmation of Van Vleck's theory, largely owing to its band spectrum furnishing accurate term assignments. Its doublet width is comparable with kT, and on spectroscopic notations the normal state of the NO molecule is a regular $^2\Pi$ doublet of width $h\Delta\nu$, equal to 120·9 cm.$^{-1}$ or 124·4 as quoted by Mulliken, Jenkins and Barton.[52] For high temperatures with kT large compared to the multiplet intervals the value of the effective magneton number for NO can be calculated by the help of equation (44), by taking $S=1/2$, $\Lambda=1$, in

$$\mu^2_B=[4S(S+1)+\Lambda^2]$$

which comes out to be 2. When multiplet intervals are large (say at low temperatures) compared to kT, Van Vleck has used the expression

$$\chi_M=\frac{N\beta^2}{3kT}(\Lambda+2\Sigma)^2 \tag{46}$$

At low temperatures the effective magneton numbers can be calculated by substituting for $\Sigma=-\frac{1}{2}$ and $\Lambda=1$ in equation (46). This gives it a magneton number zero at low temperatures. The experimental value for the magneton number from the value of χ_M for NO has already been shown to be 1·86, which is intermediate between the two asymptotic values just calculated.

Van Vleck[53] has tested the theory in a very rigid manner for the intermediate case and has shown that the effective Bohr magneton number is the following function of temperature

$$\mu_B=2\sqrt{\left(\frac{1-e^{-x}+xe^{-x}}{x+xe^{-x}}\right)}$$

where

$$x=\frac{h\Delta\nu}{kT}=\frac{173}{T}$$

At 20° C. the calculated value of the effective Bohr magneton number comes out to be 1·836. This is within 1 per cent. error of the experimental value 1·86 and is not to be considered excessive on account of the experimental difficulties and because the theory itself has several small approximations. The predicted dependence of the magneton values on temperature has been recently tested by a host of workers and is a wonderful triumph for the Van Vleck formula. Some of the more notable results are shown in the following table.

TABLE VII

CALCULATED AND OBSERVED MAGNETON NUMBERS FOR NO AS A FUNCTION OF TEMPERATURE (VAN VLECK)

Temp. °C.	μ_B Calc.	μ_B Obs.	Temp. °C.	μ_B Calc.	μ_B Obs.
−273·0	0·0	..	−34·6	1·794	1·794 (W., deH. and C.[54])
−223·0	1·098	..	−22·4	1·807	1·807 (St.[55])
−173·0	1·489	..	16·2	1·833	1·841 (St.)
−160·2	1·546	1·535 (W., deH. and C.)	17·2	1·834	1·834 (Ah. and S.[56])
−137·5	1·624	1·627 (St.)	19·1	1·836	1·852 (W., deH. and C.)
−115·8	1·678	1·679 (St.)	23·0	1·837	1·837 (Bit.[57])
−107·6	1·695	1·691 (W., deH. and C.)	77·0	1·864	..
−95·0	1·718	1·713 (St.)	227·0	1·908	..
−78·3	1·744	1·732 (Ah. and S.)	727·0	1·955	..
−57·0	1·771	1·768 (Bit.)	∞	2·000	..

Other gases which have been definitely shown to be paramagnetic are NO_2, ClO_2 and liquid ozone.

A large number of complex compounds, particularly of the transition group of elements, are paramagnetic. They have provided a very interesting field of study both on the classical and the wave mechanical principles. A more or less complete account of their behaviour is given in Chapter IX.

15. DIA- AND PARAMAGNETIC EFFECTS DUE TO FREE ELECTRONS

The theory of electrical conduction in metals due to Drude and others required large numbers of free electrons which move about among the atoms of the metal in a similar manner to the molecules in a gas. The presence of these free electrons was made to account for the diamagnetic behaviour of metals in a theory given by Schrödinger[58] in 1912. This theory depends upon the fact that electrons moving about freely like the molecules of a gas will have their paths curved in the presence of a magnetic field and the curvature would be in a sense to show a diamagnetic effect. A simplified theory of the same effect was given in 1920 by H. A. Wilson[59]. Wilson considered the case of a cylindrical metal bar with an impressed magnetic field along the axis of the cylinder. For a large number n of electrons contained in a unit volume and all moving with the same velocity V and describing free paths, the total angular momentum about the axis due to the presence of the field is given by

$$\Sigma p = -\tfrac{2}{3}\,\frac{nm\omega\lambda^2}{1+\omega^2 T^2}$$

where m=mass of the electron, $\omega = \frac{eH}{m}$ and $\lambda = VT$, T being of the order of the time taken in a mean free path.

Wilson derived for the volume susceptibility the relation

$$\kappa_f = -\tfrac{1}{3}\,\frac{ne^2\lambda^2}{m(1+\omega^2 T^2)}$$

or since under normal conditions $\omega T \ll 1$

$$\kappa_f = -\tfrac{1}{3}\cdot\frac{ne^2\lambda^2}{m}$$

In the above equation $n\lambda$ and λ were estimated from measurements on electrical conductivity and atomic volumes. The theory was not in accord with the experimental diamagnetic values for metals and it was considered that free electron diamagnetism could exist side by side with the Langevin dia- or paramagnetism due to orbital motion of the electrons.

The above derivation of free-electron diamagnetism has been criticised by Bohr[60], Miss van Leeuwen[61], and Van Vleck[62]. Due to the effect of the boundary electrons which will have an angular momentum in a reverse direction to that of the inner electrons, it has been shown that on Schrödinger-Wilson treatment there should be no diamagnetic effect at all.

Landau[63] has revived the free-electron diamagnetism by his interesting application of quantum mechanics to the problem.

The difference in the classical and quantum mechanical calculations arises from the fact that whereas in the former case all the electronic velocities obey the Maxwell-Boltzmann distribution law, in the latter case application is made of the Fermi-Dirac statistics and the inner and the boundary electrons are endowed with different quantised velocities. As a consequence the magnetic moments do not compensate and the resultant susceptibility, according to Landau, comes out to be one-third of that calculated by Pauli for free-electron paramagnetism (see next paragraph).

Pauli[64] has applied Sommerfeld's conduction theory of free electrons to the calculation of the susceptibilities of metals. The electrons in the new theory are still considered to form practically a perfect gas, but their distribution is non-Maxwellian owing to their small mass. The electron gas is regarded as degenerated ideal gas obeying Fermi-Dirac statistics. On the assumptions that the magnetic properties are due to the free electrons in the metals and that the electron possesses a magnetic moment by virtue of its spin, Pauli derives an expression for the volume susceptibility of the electron gas, viz.

$$\kappa=4\left(\frac{\pi}{6}\right)^{\frac{2}{3}}G^{\frac{2}{3}}\frac{\mu^2 n^{\frac{1}{3}} m}{h^2}\ (\text{for } T=0^\circ \text{ abs.}) \quad . \quad . \quad (47)$$

in which $G=(2J+1)$ is the 'statistical weight' and μ is the effective electronic magnetic moment given by $\mu=\beta g\sqrt{J(J+1)}$, g being Lande's splitting factor and β the Bohr magneton.

For the particular case of the alkali metals which have one valence electron Pauli identifies the valence electron with the free electron and thus finds for the number of free electrons the same number as the atoms present in the metal. Also, on the spectroscopic data the ions of the alkali metals should have zero magnetic and spin moments and as such should behave as diamagnetics. Consequently on Pauli's calculation the feeble paramagnetism shown by the metals is entirely due to the valence electrons behaving as free electrons and responsible also for the electrical conductivity.

For the alkali metals the constants in Pauli's equation will be given by $J=1/2$, $g=2$, hence $G=2$ and $\mu=\sqrt{3}\beta$; taking m, the mass of the electron $=9{\cdot}03\times 10^{-28}$, equation (47) reduces to

$$\kappa_v=n^{\frac{1}{3}}.\,2{\cdot}20\times 10^{-14} \quad . \quad . \quad . \quad (48)$$

Further, the value of the volume susceptibility, though deduced for absolute zero, remains practically unchanged up to room temperature. This accords with the known fact that in alkali metals the susceptibility is practically independent of temperature. According to McLennan's results [65] the susceptibilities of the alkali metals are approximately constant from − 190° to about the temperature of the melting-point, at which point there is an abrupt but small decrease and above it a slight progressive increase with temperature.

Pauli's calculated results are given in Table VIII against the latest values due to Lane [66].

For a complete expression for the susceptibility it is necessary to take into account (i) the diamagnetic effects of the atom cores, and (ii) the diamagnetic effect arising from Landau's free electron diamagnetism. Of these (i) has been calculated from screening constants or magnetic data and (ii) has the magnitude of one-third of Pauli's value but of opposite sign. The corrected values are also given in Table VIII.

TABLE VIII

CALCULATED AND OBSERVED SUSCEPTIBILITIES OF ALKALI METALS

$\chi_A \times 10^6$

Alkali Metal	χ Pauli	χ_i Atom Core Diamagnetism	χ_{ii} Landau's Diamagnetic Correction	χ_A Pauli Corrected	χ_A Lane Experimental
Na	15·6	−4·2	−5·2	6·2	15
K	23·6	−16·7	−7·9	−1·0	21
Rb	27·2	−31·3	−9·0	−13·1	18
Cs	32·3	−45·7	−10·8	−24·2	29

NOTE.—For atom core diamagnetism Pauling's calculated values [67] have been used for Na^+ and K^+ as better suited for light atoms. Ikenmeyer's values [68] used for Rb^+ and Cs^+ have been calculated from magnetic susceptibility data by additivity method.

The agreement between Pauli's original values and the experimental data then available and latterly those of Lane was very satisfactory, and for a time it appeared to completely explain the feeble paramagnetism of the alkali metals. The corrected Pauli values are entirely at variance with the experimental results, and if the magnitude of the corrections could be relied upon, Pauli's calculations lose all their significance.

Leaving aside the case of metals it would be interesting to apply Pauli's theory to those crystals and crystalline aggregates which show a marked photo-electric conductivity. In such substances also, it is supposed that the conductivity arises from free electrons.

16. BLOCH'S EXTENSION OF THE PAULI FORMULA

By substituting the values of G, g, J for alkali metals and multiplying by $\frac{1}{V}$ in order to convert the volume susceptibility into the specific susceptibility equation (47) assumes the more familiar form of the Pauli formula for the alkali metals:

$$\chi = 12m\beta^2\left(\frac{n}{V}\right)^{\frac{1}{3}}\left(\frac{\pi}{3}\right)^{\frac{2}{3}} \quad . \quad . \quad . \quad (49)$$

Bloch[69] has improved this formula by considering a second approximation in the Fermi-Dirac statistics of free electrons:

$$\chi = \beta^2\left[\frac{12m}{h^2}\left(\frac{n}{V}\right)^{\frac{1}{3}}\left(\frac{\pi}{3}\right)^{\frac{2}{3}} - \frac{64\pi^4 V m^3 k^2 T^2}{9nh^6}\right]$$

$$= 2{\cdot}20 \times 10^{-14}\left(\frac{n}{V}\right)^{\frac{1}{3}} - 1{\cdot}03 \times 10^7 T^2 \frac{V}{n} \quad . \quad . \quad (50)$$

$\left(\frac{n}{V}\right)$, the number of conduction electrons per unit volume, is of the order 10^{22}, so the second term is negligible as compared to the first one at ordinary temperatures and the formulae (49) and (50) give almost identical values. The independence of temperature predicted by equations (49) and (50) is borne out by the experimental results of McLennan, Ruedy and Cohen.[65]

17. EXPERIMENTS OF GERLACH AND STERN ON THE MAGNETIC DEVIATION OF ATOMIC RAYS

Long before the theory of Hund and Van Vleck was in the field Gerlach and Stern[70] had experimentally established the presence of discrete magnetic moments in atoms. A straight beam of vapour consisting of silver atoms was passed through a non-homogeneous magnetic field and was found to be split into two components. If all positions of the atoms with respect to the magnetic fields were possible the original beam must have been somewhat deflected as a whole and should have shown a general broadening rather than an explicit splitting into two components.

A diagrammatical representation of the apparatus employed by Gerlach and Stern is shown in Fig. 35. The element to be investigated was placed in a furnace F in which a high vacuum could be maintained. The furnace was heated to a temperature higher than the melting-point of the metal and the whole apparatus was highly evacuated. The metal vapour escaped through the aperture A and passed through two limiting diaphragms S_1 and S_2 forming a narrow pencil of molecular (or atomic) rays. The rays then passed between the poles of a powerful magnet MM which produced a non-homogeneous field with steep gradient along the vertical of the figure by means of the special pole-pieces of the wedge-grove type shown separately in Fig. 36A and B. The atoms were finally deposited on a glass plate and remained invisible to the eye until 'developed' by placing in a hydroquinone-silver nitrate developing solution. This process worked satisfactorily for silver, gold, copper, tin and nickel. With bismuth, antimony, iron and lead it was difficult to obtain a good trace. The process had therefore to be modified according to the difficulties experienced, and recourse was taken to microphotography when chemical methods showed difficulties of manipulation, particularly in elements requiring high temperatures of vaporisation on account of the deposition of mercury and grease on the plate. The essential parts of the apparatus were not large. In most cases the pole-piece was only 5 cm. long. The furnace was 2 cm. long, the plate P which received the atoms was 3 mm. square and the distance between the knife-edge and the plane of the slotted pole-piece was approximately 1 mm.

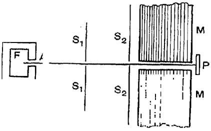

FIG. 35.—Gerlach and Stern experiment.

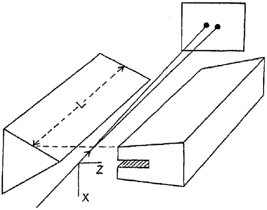

FIG. 36A.—Gerlach and Stern experiment, showing the path of the atomic rays through the magnetic field.

High vacuum is essential for the experiment, and liquid air and charcoal were employed. Great care was required to keep the temperature, the vacuum and the magnetic field constant. In preliminary experiments four to five hours were necessary, but with the perfecting of the technique this period was reduced to about forty-five minutes.

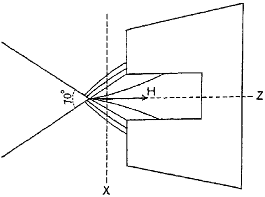

FIG. 36B.—Gerlach and Stern experiment (enlarged view of the pole-pieces).

The inhomogeneity of the field $\frac{\delta H}{\delta z}$ was determined from separate measurements of H and $H\frac{\delta H}{\delta z}$. The field H was measured by means of a bismuth spiral and the values of $H\frac{\delta H}{\delta z}$ were obtained by measuring the repulsion at various points of a thin bismuth wire suspended in the field by a delicate frame of quartz so arranged that the couple due to the force of repulsion on the bismuth wire $\left(\text{proportional to } KH\frac{\delta H}{\delta z}\right)$ could be counterbalanced by that produced by placing riders on a transverse arm of the frame.

We shall discuss the case of silver. In this case the original beam was split into two components. Let the magnetic moment of the atom be denoted by μ, the field strength by H and the field gradient by $\frac{\delta H}{\delta z}$. This gradient is directed in the same direction as H and is normal to the path of the atom.

Let the magnetic axis of the atomic magnet make an angle θ with the direction of H, then the force acting on the magnet will be given by $\mu \cos \theta\frac{\delta H}{\delta z}$. This will be equal to $\mu_H\frac{\delta H}{\delta z}$, where μ_H is the component of μ resolved along the field. If the atoms in the beams have a mass m and a velocity v through a path of length L where the field gradient has the same value, then the displacement s of the atomic ray at right angles to its direction of motion is given by

$$s=\frac{\delta H}{\delta z}\left(\frac{L}{v}\right)^2\times\frac{1}{2}\frac{\mu_H}{m}$$

Under rigid control of pressures the velocity of the atoms will depend upon the temperature of vaporisation of the metal, i.e.

$$\tfrac{1}{2}mv^2=\tfrac{3}{2}kT$$

or

$$v=\sqrt{3}\sqrt{\frac{kT}{m}}$$

where k is the Boltzmann constant and T the absolute temperature.

In actual experiments the mean velocity of atoms passing through the slit was greater and was given by $\sqrt{4}\sqrt{\frac{kT}{m}}$. The average value adopted was therefore $\sqrt{3{\cdot}5\frac{kT}{m}}$. In the case of silver the deflection s was carefully measured on the plate and from the above expression the value of μ_H was calculated to be ± 1 Bohr magneton.

Thus Stern and Gerlach found complete agreement between the observed and calculated deviation. In 1924 the experiments were repeated with copper and gold; a value of one Bohr magneton was obtained for the atomic moments of these elements. The atomic rays of cadmium, mercury, lead, tin and zinc did not show any deflection in the magnetic field and the natural conclusion from this is that they do not carry a magnetic moment. Bismuth gave a ray which showed considerable amount of deviation towards the pole-edge and an undeflected ray of zero magnetic moment. Thallium also showed a magnetic moment of one-third of a magneton. The scope of this book does not permit a detailed discussion of these results, but they form an excellent support for the present views on atomic structure. The deviations can be predicted on the theory of the anomalous Zeeman effect with a knowledge of the multiplet separation and Lande's g-factor, as already treated in Chapter V, Section 19. The Lande g-factor and Mg values for different normal states, and also a sketch of the expected atomic ray patterns as arrived at from a knowledge of spectroscopic normal terms, are given in Table IV of the chapter.

Phipps and Taylor [71] and Wrede [72] have repeated the experiments using a hydrogen discharge tube as a source of mono-atomic hydrogen. A plate coated with molybdenum trioxide acted as a recording screen and this when reduced by atomic beam of hydrogen gave blue lines on a white background. Two reduced areas were distinctly seen under the measuring microscope and the measured distance agreed with the calculated values, showing that the hydrogen atom had a magnetic moment of one Bohr unit as required by theory.

This result is of particular interest as on the newer quantum theory the electric field of the hydrogen atom in the normal state possesses spherical symmetry and should under all conditions exhibit perfect isotropy in collision with other atoms. This would lead to the conclusion that in the normal state its magnetic moment should be zero, but as it shows a value of ± 1 magneton it is evident that the spin must be taken into account. It is, in fact, the spin momentum vector which orientates in the case of hydrogen.

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CHAPTER VIII

FERROMAGNETISM

PERHAPS the subject of ferromagnetism constitutes the most important and the most perplexing study in the domain of magnetic phenomena. The earliest history of the whole subject is intimately connected with iron and some, though not all, of its compounds, and with allied elements like nickel and cobalt and with a series of such substances as the Heusler alloys and compounds of the type of manganese arsenide, antimonide, nitride, bismuthide and phosphide. Not only does the iron which is chemically pure come under this class of substances, but also iron in combination with other elements, particularly carbon, silicon, manganese, tungsten, chromium, nickel and cobalt, is to be considered as ferromagnetic material. The quantities of these elements play an important rôle in determining the magnetic properties of this metal. Further, these properties are influenced by the history, mode of formation, the mechanical effects such as forging, casting and rolling and the previous thermal treatment of the element.

1. CAST IRON—INFLUENCES OF IMPURITIES

The increasing application of cast iron in the construction of electrical machinery has evoked a more intimate knowledge of the magnetic properties of this material. The magnetic properties, like electrical resistance, may vary widely, ranging from materials having low permeability and high coercive force, suitable for permanent magnets, to those having high permeability, low coercive force and low hysteresis loss suitable for electrical machinery.

A series of extensive investigations have been carried out by numerous workers to study the effect of heat treatment and carbon content for production of high-class magnet steel. Partridge[1] has studied the influence of the various elements on the magnetic properties of cast iron. His main conclusions are:

(i) Annealing increases magnetic induction and permeability.

In some extreme cases the magnetic induction could increase by 70 per cent. and the maximum permeability ten-fold.

(ii) Phosphorus has little effect on the magnetic properties of cast iron.

(iii) In the case of cast iron silicon decreases the magnetic induction, but its presence may be advantageous in alloys which have to work at low flux densities, e.g. transformer cores.

(iv) When high permeability is required graphite should be in the form of temper carbon, as little combined carbon as possible should be present, and free cementite must be absent.

(v) Silicon reduces the coercive force and the hysteresis loss.

(vi) Manganese, nickel and chromium are prejudicial to high magnetic induction.

(vii) In the annealed condition Mn and Cr increase the coercive force and hysteresis loss and decrease the remanent magnetism.

(viii) Cobalt increases the magnetic induction, the remanence and the maximum permeability.

(ix) In the cast state aluminium decreases the magnetic induction, permeability and remanent magnetism and increases the coercive force and the hysteresis loss, but in the annealed condition up to 1 per cent. aluminium decreases the magnetic induction and the maximum permeability, but increases the coercive force and the hysteresis loss. When present in amounts from 1 to 3 per cent., however, aluminium causes a very large decrease in induction and permeability, coercive force and hysteresis loss.

Further, Moir[2] has found that 8 per cent. tungsten and chromium steels have large residual magnetism and high coercive force and are very suitable for permanent magnets. In 1920 Honda and Saito[3] discovered a cobalt steel which had remarkably high coercive force. By studying the magnetisation curves of various alloys, and in particular the effect on these curves when special heat treatment is applied to metals, it has been possible to find alloys which will give particular magnetic properties. This is illustrated by the discovery of permalloy and perminvar. Recently Dawson[4], of Messrs. Ferranti Ltd., has evolved a non-magnetic cast iron containing 10 per cent. nickel, 5 per cent. manganese and 1 per cent. aluminium. It has a very low permeability and a very high electrical resistivity. The casting, machining and tensile properties are similar to those of cast iron, with the advantage of increased toughness. This material should, therefore, find a fruitful application in the construction of alternators and other electrical machinery such as end-plates, shields for generators and motors, transformer covers, cable boxes, resistance grids, etc.

A whole treatise can be written on the subject, but it will suffice here to indicate briefly in the table given below the characteristic features of changes brought about in the properties of iron under varying physical and chemical influences.

TABLE I

MAGNETIC PROPERTIES OF IRON IN DIFFERENT STATES

κ (susceptibility) $=a+b\text{H}$

Material	H (limits) *	$4\pi b$	$4\pi a$
9c Electrolytic iron, unannealed	..	8·5	102
9a Electrolytic iron	..	1358	628
9a Electrolytic iron	..	..	754
9 Electrolytic iron aged at 130° C.	..	176	201
Tungsten steel, annealed	0·1 to 3·1	3·1	112
Tungsten steel, quenched	0·1 to 3·5	0·4	28
Cast iron	0·1 to 4·0	3·0	40
Cast steel	0·07 to 0·9	168	235
Iron sheets	0·07 to 0·75	1106	569

* Limits of H within which the formula $\kappa=a+b\text{H}$ holds.

2. TEMPERATURE AND FERROMAGNETISM

The most important feature of the ferromagnetic substances is that at high temperatures, corresponding to or above the Curie point, they lapse into paramagnetics. This may be illustrated by plotting the susceptibility-temperature curve. The curves for iron, cobalt and nickel are shown in Fig. 37. Other features of these elements are indicated in Table II.

TABLE II

CONSTANTS FOR FERROMAGNETIC SUBSTANCES ABOVE CURIE POINT

Ferromagnetic Substance	Temperature Range °C.	θ	Curie Constant	Bohr units, μ_B	Weiss units, p
$\text{Fe}\beta_1$	774-828	1047	2·21	4·2	20·9
$\text{Fe}\beta_2$	828-920	1063	1·53	3·5	17·4
$\text{Fe}\gamma$	920-1395	– 1340	4·03	5·7	28·2
$\text{Fe}\delta$	1395- . . .	1543	0·251	1·4	7·05
$\text{Co}\beta_1$	1170-1241	1404	1·28	3·2	15·9
$\text{Co}\beta_2$	1241-1303	1422	1·07	2·9	14·55
$\text{Ni}\beta_1$	412-900	645	0·325	1·6	8·02

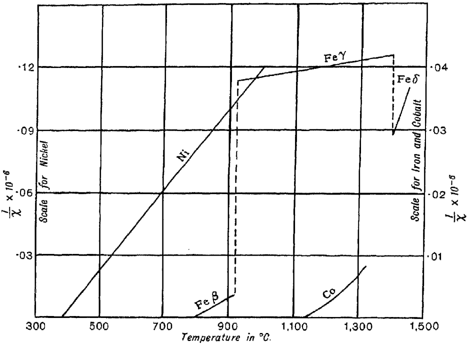

FIG. 37.—$1/\chi$-T curve for Fe, Ni and Co, above Curie point.

3. B-H RELATIONS

Besides the thermal variation of susceptibility and the existence of the Curie point the characteristic permeability and B-H curves indicate the nature and quality of these ferromagnetic substances. The B-H curves for various types of iron and for cobalt, nickel and an iron cobalt alloy are shown in Fig. 38.

Several interesting points emerge from these results. For example, it is seen that for electrolytic iron when $H = 2000$ gauss the induction density B is equal to 23,600. At this density this iron becomes saturated. The difference in behaviour of iron other than the electrolytic iron is also prominently brought out. Particularly noticeable is the extraordinary result regarding the saturation intensity of magnetisation of the iron-cobalt alloy Fe_2Co which exceeds remarkably the value for pure iron. This property enhances the value of this alloy as a material for use in electromagnets, motor generators and dynamos.

4. FERROMAGNETIC ALLOYS AND THEIR COMMERCIAL APPLICATIONS

Reference has already been made to alloys of iron containing small quantities of certain elements. Some alloys of iron

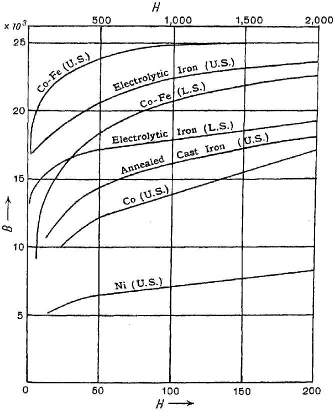

FIG. 38.—B-H curves for some ferromagnetic materials.
U.S.=upper scale for H. L.S.=lower scale for H.

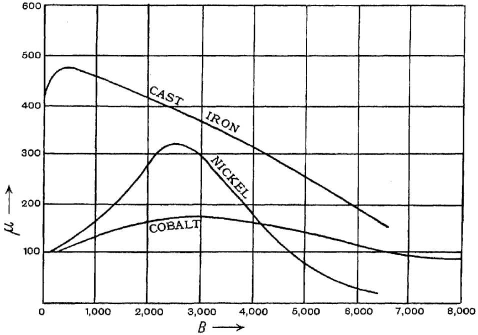

FIG. 39.—B-μ curves for iron, nickel and cobalt.

with other elements have acquired importance because of their use for electrical engineering purposes. For example, it has been noticed that if a small percentage of silicon is added to commercially pure iron the physical properties of the alloy so formed undergo profound changes. The electrical resistance is greatly increased and so is its permeability over a wide range of induction densities, while the hysteresis loss is reduced very considerably. Sir R. A. Hadfield has prepared an alloy well known commercially as 'stalloy'. Its constituents are iron, silicon, manganese, sulphur, carbon and phosphorus. The alloy is remarkably good for making electromagnets and electrical motors. By reducing the percentage of silicon the disadvantage of brittleness of this alloy can be got over, though at the expense of its magnetic advantages. Another use of specially treated iron is in the manufacture of permanent magnets. The best steels for making permanent magnets are: (*a*) the tungsten magnet steel, (*b*) Japanese cobalt steel, popularly known as K.S. magnet steel, (*c*) Hadfield's 'permanite', and (*d*) cobalt chromium magnet steel.

A series of alloys of nickel and iron containing from 45 to 80 per cent. nickel is known by the name of 'permalloy'. These alloys have quite high permeabilities for low fields and they reach saturation with magnetising force less than 10 gauss. The important commercial use of these alloys is in the 'loading' of submarine cables and for obtaining the requisite distributed inductance enabling the cables to be worked at high speeds of signalling without distortion of the messages. Recently important commercial use for them has been found in the manufacture of small transformers for radio work. Other alloys of this type are known as the Mu metal and the radio metal.

Amongst ferromagnetic alloys mention must be made of the ternary alloy prepared in 1898 by Heusler[5] and known after his name as the Heusler alloy. The constituents of this alloy are aluminium, manganese and copper. There is no element of the ferromagnetic group in it at all and yet the magnetic properties resemble and occasionally exceed those of nickel. The most strongly magnetisable alloy has approximately the following composition:

Copper	70 per cent.
Manganese . . .	20 per cent.
Aluminium . . .	10 per cent.

It has been shown that aluminium can be replaced in these alloys by bismuth, arsenic, tin, antimony and boron without much loss of the ferromagnetic properties. The ferromagnetism in this alloy is attributed to a chemical complex of the composition $[Al(Mn.Cu)_3]x$. Other binary compounds which show ferromagnetism are Mn_3Al, $MnAg_2$ and Mn_4Sn. Curie points have been established for the following compounds which also exhibit ferromagnetism:

	Curie Point, °C.
MnBi . . .	360-380
MnSn . . .	320-330
MnAs . . .	40-45
MnP . . .	18-25

5. WEISS MOLECULAR FIELD THEORY: SPONTANEOUS MAGNETISATION

The important earlier theories of magnetism which form a previous chapter in this book refer to ferromagnetic substances and much of the important work on the subject is due to Ewing, Evershed and Swinburne. The molecular magnetic hypothesis in the hands of these workers has been able to account for the general phenomenon of hysteresis. The explanation is, however, pictorial and not quite quantitative. The next attempt to explain ferromagnetism satisfactorily is due to Weiss, who introduced in Langevin's theory of paramagnetism the idea of an internal or molecular field proportional to the intensity of magnetisation acquired.

According to this postulate the internal molecular field H_i should be proportional to the intensity of magnetisation I, i.e.

$$H = H_e + H_i = H_e + nI$$

where H = effective field, H_e the external field and n = a constant dependent upon the nature of the substance.

This theory has already been considered in relation to paramagnetic substances and was found to afford a better relation in most cases. In the case of ferromagnetics, if the origin of the internal field was taken to be entirely magnetic the value of n should be about $4\pi/3$. The observed susceptibilities in ferromagnetics, however, are very much greater than could be accounted for on this value and are also occasionally negative. H_i, 'the internal molecular field', may therefore be regarded as an interaction field whose origin is unexplained, but in effect it is equivalent to a magnetic field proportional to I.

The Weiss theory considers the effect of the internal molecular field by dividing the molecular magnets in small groups or 'domains' of the order of magnitude of the microcrystals constituting the ferromagnetic metal. Within each of the 'domains' the same assumption is made that the internal molecular field is proportional to intensity of magnetisation, i.e. $H_i = nI$. When n is positive there arises a probability for spontaneous magnetisation even in the absence of any external field. As given in equation 8, Chapter VII,

$$\frac{\bar{\mu}}{\mu} = \left(\coth a - \frac{1}{a}\right)$$

or for a gram-molecule

$$\frac{\sigma}{\sigma_0} = \coth a - \frac{1}{a} \quad . \quad . \quad . \quad . \quad (1)$$

where

$$a = \frac{\mu H}{kT}$$

In the absence of the external field $H_e = 0$, and if M is the molecular weight and ρ the density of the substance,

$$a = \frac{\mu H_i}{kT} = \frac{N\mu}{Nk} \cdot \frac{nI}{T} = \frac{\sigma_0}{R} \cdot \frac{n}{T} \frac{\rho\sigma}{M} = \frac{\sigma_0^2 n \rho}{MRT}.$$

Hence

$$\frac{\sigma}{\sigma_0} = \frac{MRT}{\sigma_0^2 \rho n} \cdot a \quad . \quad . \quad . \quad . \quad (2)$$

The magnetic state of the material at any temperature will be determined by the simultaneous equations (1) and (2). These equations can easily be solved graphically, as in the figure, where the values of σ/σ_0 are plotted against a. The equation (1) gives the Langevin curve (i) and equation (2) gives a straight line passing through the origin (ii). The slope of this line increases with temperature T.

The curves intersect at the origin and at the point A where $a = a'$. As the temperature rises the slope of curve (ii) will rise, and consequently a' will diminish till at a certain critical temperature $a'' = 0$ and the line (ii) will then become tangential with the curve (i). At this point since $a' = 0$, the slope $= 1/3$ (according to Langevin equation for a small). This critical temperature corresponds to that at which the ferromagnetic properties disappear.

For temperatures lower than the critical temperature

$$\frac{\mathrm{MRT}}{n\rho\sigma_0^2} < \tfrac{1}{3}$$

or

$$\mathrm{T} < \frac{n\rho\sigma_0^2}{3\mathrm{RM}} < \theta \quad . \quad . \quad . \quad . \quad (3)$$

where θ denotes the limiting temperature at which spontaneous magnetisation just becomes possible. At higher temperatures the effect of thermal agitation is enough to overcome any tendency for the magnetic molecules towards spontaneous alignment and the substance behaves as a normal paramagnetic.

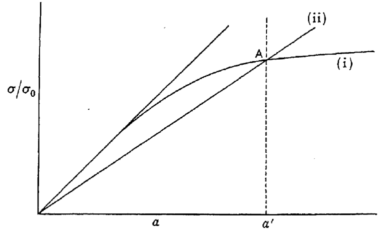

FIG. 40.—Langevin curve, showing spontaneous magnetisation at a.

At lower temperatures the Weiss 'domains' within the substance should possess the full magnetisation given by the intersection of the curves, though they may be randomly orientated and show no resultant field.

A point in support of the theory of spontaneous magnetisation was afforded by the discovery by Weiss and Beck[6] of the magneto-thermal effect. When a ferromagnetic substance is suddenly inserted into a magnetic field the magnetisation produced is accompanied by a reversible change of temperature, and it follows on thermodynamical reasoning that an adiabatic rise $\Delta\mathrm{T}$ in temperature results according to the equation

$$\Delta\mathrm{T} = -\frac{\mathrm{T}}{\mathrm{S_H}} \cdot \frac{d\mathrm{I}}{d\mathrm{T}} \cdot \Delta\mathrm{H} \quad . \quad . \quad . \quad (4)$$

where $\Delta\mathrm{H}$ is the change in field and $\mathrm{S_H}$ the specific heat in a constant field. An adiabatic fall of temperature by the same amount should occur if the field is removed suddenly. Since $\frac{dI}{dT}$ has a maximum value at the Curie point, the change in temperature should be the maximum at that point. The specific heat calculated for nickel from equation (4) agreed well with calorimetric measurements. An equation for measuring the change ΔS at the Curie point was given by Lorentz[7] which made it possible to calculate the change at the temperature where its magnitude is the largest.

Following Heisenberg's theory of ferromagnetism, Fowler and Kapitza[8] have developed a theory of the specific heats of ferromagnetic substances. This theory predicts a decrease in the specific heat by about three calories per gram-molecule per degree at the Curie point. For manganese arsenide the change given by Weiss theory and confirmed by experiment is of the order of 100 cals. per gram-molecule per °C. Agreement for nickel appears to be better. Sucksmith and Potter's[9] experimental values range between 0·9 to 1·34 cal./gm. mol. per °C. Dorfmann, Jaanus and Kikoin[10] have made the interesting suggestion that the lowering in the specific heat at Curie point may be ascribed partly to the positive ions and partly to free electrons.

Some confirmatory evidence regarding the molecular field of Weiss is obtainable from the experiments of Maurain[11] on thin films. He found that in a magnetic field which is in the plane of the film the magnetic moment of the iron deposited electrolytically increased proportionately to the thickness when this exceeded 80 $\mu\mu$. On changing the direction of the field and decreasing its strength (about 1·65 gauss) which did not exceed the coercive field the magnetic moment of the film on further deposition continued to increase in the initial direction, evidently on account of the influence of the molecular field.

6. MODERN THEORIES OF FERROMAGNETISM *

Theory of Gans.—A theory of ferromagnetism has been developed by Gans[12]. He postulates that magneton or an elementary magnet is an electrified body of revolution rotating rapidly about its axis of figure. A group of such magnetons constitutes the elementary magnet, and further it is assumed that these magnetons are distributed through space according to the laws of probability, which has the figure of ellipsoid with three unequal axes and free to move about within the complex. A ferromagnetic crystal is composed of such complexes placed in such a manner at the intersection of a space lattice that their corresponding axes are parallel.

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* We are indebted to the article by McKeehan in *Reviews of Modern Physics*, 2, 477 (1930), which contains an excellent account of the modern theories of ferromagnetism.

By the application of statistical mechanics to the system of such complexes, relations similar in form to those of Weiss but more easily understandable and more accurate have been derived between susceptibilities and temperature. Another achievement of this theory is that from stability considerations Gans has been able to satisfactorily account for the variation of coercivity with temperature and to calculate the number of magnetons in a unit volume as well as the magnetic moment per magneton. The theory differs from that of Weiss only in this respect that in the Weiss theory the effective field (H) acting at a definite point within a ferromagnetic substance consists of two parts, the external field H_e and the molecular field H_i, while in the Gans[13] theory it consists of three parts:

(*a*) The external field H_e,

(*b*) The structural field (equal to $\frac{4}{3}\pi I$),

(*c*) A molecular field due solely to action of magneton of the particular complex.

This theory ignores the crystalline character of the medium as well as hysteresis, but Gans has more recently proposed another theory to account for the magnetisation of polycrystalline metals. In computing the magnetisation curves and hysteresis loops the effective field within each 'crystallite' is considered in three parts: (i) the applied field, (ii) the field due to the combined action of remote parts of the specimen, and (iii) the field due to adjacent 'crystallites'. The direction and magnitude of the (iii) component alone has different values from point to point, which accounts for the different values of applied field and of average magnetisation at which discontinuities occur.

Heisenberg.—The interchange of electrons in atoms which is characteristic of quantum mechanics has been shown by Heisenberg[14] as capable, under certain conditions, of giving rise to those effects which have been partially explained on the molecular field theory.

In this theory Heisenberg has investigated the effect of interchange interaction in a lattice of similar atoms, each atom containing one electron capable of free rotation. Magnetisation is supposed to be due to these electrons and the remainder of the atom is supposed to have no magnetic effect. It is shown that if the interaction integral has a positive sign spontaneous magnetisation may occur below a certain critical temperature, resulting in the characteristic behaviour of a model ferromagnetic material.

It is not possible to enter into the details of this highly mathematical theory, but it is desirable to discuss the general idea, and in order to do that we shall take into consideration the interaction of two normal atoms of hydrogen.

At a given distance apart a system constituted of two hydrogen atoms would show two different types of possible energies, one corresponding to an attraction and the other to a repulsion (cf. Chapter IX). As compared to the magnetic energy arising from the electron spins the magnitude of the difference in energy of these two states must be much larger. In the state of lower energy the electronic orbits are antiparallel, while in the other they are parallel. Similarly in the ideal ferromagnetic substance the energy will depend indirectly on the mutual orientation of the electronic orbits in neighbouring atoms. The electron interchange is not an actual transfer of an electron from one atom to the other, as the term interchange might seem to suggest, but it is only a mutual effect between two electrons, one in the first atom and the other in the second atom.

By applying an elaborate group theory and statistical treatment the problem of the crystal as a whole has been considered and expressions have been deduced for the variation of magnetisation with temperature and for the Curie point in terms of the interchange interaction and the number of neighbours surrounding each atom. Stoner[15] has shown that although the Heisenberg treatment leads to an expression of the type deduced on the Weiss molecular field hypothesis, yet when examined in detail the theory breaks down. Stoner has further considered the atoms in a crystal as separate systems interacting with neighbouring atoms, and deduced a much simpler treatment of the interchange interaction theory of ferromagnetism. The method differs from that of Heisenberg, who considers the whole crystal as a single system. The terms which make the original formulae unsatisfactory as a representation of the experimental results also disappear. The final expressions for the magnetisation energy are formally equivalent to those given by the Weiss theory if the classical assumption of continuous orientations of the carriers is appropriately modified and the agreement with the observations on ferromagnetics is very satisfactory.

Bloch's Theory of Free Electrons.—Bloch[16] has given a modification of Heisenberg's theory on the assumption that the electrons whose exchange effects result in ferromagnetism are not the bound but the free electrons. Assuming that for every atom there is one free valence electron and that the temperature is below the critical degeneracy temperature of Sommerfeld theory, Bloch calculates and shows that the interatomic distance on this view could not be less than $0 \cdot 22\ h^2/me^2 = 0 \cdot 5 \times 10^{-7}$. Although it is only a rough approximation, it is remarkable that for alkali metals which are only feebly paramagnetic the interatomic distances are much less than this critical value. This gives an insight into the possible mechanism of the feeble paramagnetism of these elements.

According to Bloch, free electrons will exhibit ferromagnetism only if the tendency towards ferromagnetism succeeds in overcoming the tendency of the Pauli exclusion principle or the Fermi statistics to defeat the spin paramagnetism of free electrons. Stoner[17] has criticised the view that free electrons may be the cause of ferromagnetism, as a necessary outcome of this view would be to give Curie-points values much higher than the critical temperature of the Sommerfeld conduction theory. This would yield absurdly high values for the Curie points.

Slater's Contribution.—Slater[18] has done very creditable work in deducing a reason for the unique position of iron, cobalt and nickel as ferromagnetic elements. He has imported into the Heisenberg theory the idea that the probability of interaction increases as the ratio of interatomic distance to radius of incompleted electron shell increases. This affords a very satisfactory explanation also of the ferromagnetism of Heusler's alloys. The assumption is that in compounds of the type Mn_3X where X is any trivalent metal, when copper replaces manganese, it must be so highly ionised that its incomplete three quantum shell embedded deep within its structure becomes available for the interchange interaction of the type responsible for ferromagnetism.

Stoner's Extension of the Slater Theory.—Further evidence bearing on this question has been brought forward by Stoner[19]. He has reaffirmed the view that in ferromagnetic elements the ratio (R) of inter-atomic distance ($2a$) to the sum of the effective radii ($2r_d$) of the incomplete d states is particularly large. He has also made a rough calculation of the relative interaction energy (J_0) associated with ferromagnetism of pairs of electrons in neighbouring atoms in Fe, Co and Ni. The relative values of 5·0, 8·3 and 10·5 follow the same order as the values of R, 1·63, 1·82 and 1·97. Further, the R values for unlike pairs of atoms with incomplete d shells show that they are particularly high for Co-Fe and Ni-Fe. This is due to the fact that the addition of cobalt or nickel to iron results in an increase in the average atomic moment although the atomic moment of the added elements is less than that of iron. The only non-ferromagnetic element which when added to nickel increases the average atomic moment is manganese. This fact is of considerable importance, as manganese is the element which forms the base for alloys of the type discussed by Heusler.

Mahajani.—G. S. Mahajani[20] has proposed an ingenious theory of ferromagnetism. He makes the stabilising mechanism also purely magnetic. Following Ewing, he postulates the unitary magnets to have linear dimensions comparable with interatomic distances. In order to verify his theory Mahajani uses the experimental results of Webster[21] on iron and of Weiss[22] on pyrrhotite.

In general in an isotropic medium the internal or molecular field is parallel to the intensity of magnetisation, i.e. $H_M = m . I$. In a crystal Weiss computes the molecular field H_M by taking the three components $(H_M)_x$, $(H_M)_y$, $(H_M)_z$ referred to the principal axis of magnetisation as being proportional to the components of I along these axes rather than to I itself.

$$(H_M)_x = m_x I_x$$
$$(H_M)_y = m_y I_y$$
$$(H_M)_z = m_z I_z$$

where m_x, m_y, m_z are constants.

Now in a cubic crystal one should expect $m_x = m_y = m_z$, which will show the existence of magnetic isotropy in such media. Ferromagnetic cubic crystals are, however, non-isotropic, and so Webster has suggested that the simple linear relations for

$(H_M)_x$, $(H_M)_y$, $(H_M)_z$ should be abandoned and replaced by more complicated equations. Mahajani, therefore, puts forward the following equations for cubic and non-cubic sets of crystals:

$$(H_M)_x = m_x(a_1 I_x + a_3 I_x^3 + a_5 I_x^5 + \ldots)$$
$$(H_M)_y = m_y(a_1 I_y + a_3 I_y^3 + a_5 I_y^5 + \ldots)$$
$$(H_M)_z = m_z(a_1 I_z + a_3 I_z^3 + a_5 I_z^5 + \ldots)$$

For cubic crystals only two terms need be considered. For non-cubic crystals only one term is enough.

The quantities derived from the experiments are the maximum values of the molecular field, i.e. $(H_M)_x$ for I along the x-axis, etc. Webster in his experiments obtains for this a value of the order of 500 gauss. To account for this Mahajani finds that the radius of the Weber elementary magnet should be of the order 2×10^{-9} cm., which compares favourably with the value for normal electronic orbits.

In iron the body-centred cubic space lattice may be supposed to be divided into two simple cubic space lattices with each of which the associated atomic magnets should, on Mahajani's assumption, be always all parallel to one line, while those associated with the other simple cubic lattice should be parallel to another line. Since the points of these two lattices ought to be crystallographically equivalent, there is no justification for this on chemical or physical grounds. This criticism against Mahajani's theory is, however, not formidable, as its quantitative successes belong exclusively to nearly saturated conditions in which the energies are computed simply for the complete space lattice.

Akulov's Theory.—In dealing with ferromagnetic crystals two types of forces have been taken into consideration by Akulov[23].

(*a*) The torque exerted upon each atomic magnet by the whole array; and

(*b*) The anisotropic cohesive forces which come into play when the magnets are co-directed in various crystallographic directions.

This theory does not deal with hysteresis and holds rigorously only in relatively intense magnetisation where the width of the hysteresis loop becomes negligible. If I_P is the intensity of magnetisation parallel to H_A, then, making use of an I_P-H_A curve, a distance I_S is measured along the I_P axis such that

I_S is the saturation value of I_P, and a line is drawn through this parallel to H_A axis and intersecting the I_P-H_A curve at a certain point. Akulov then measures the area included between the curve and the I_S perpendicular. This area changes as the direction of H_A is rotated about in a selected crystallographic plane containing two axes for which the direction of I is parallel to H_A. On Akulov's theory the curve connecting the measured area with the azimuth of H_A is closely reproduced. Also the theory shows a qualitative agreement with the magneto-striction phenomenon observed by Webster[24] and by Honda and Mashiyama[25] in single crystals of both iron and nickel.

A plausible assumption, although one contrary to custom, is made by Akulov in applying his theory to lower field intensities. The assumption is that in the unmagnetised state the orientations of the atomic magnets are in a state of statistical disorder, i.e. these atomic or elementary magnets point in all possible directions. A further assumption is the spatial quantisation of these atomic magnets with respect to H_A, as a result of which the local magnetic field arising from neighbouring atoms is ignored. This does not make the theory too flexible, as Akulov puts much more serious restrictions in supposing that there are not more than two stable orientations for each magnet, one parallel to H_A and the other antiparallel.

With these partially doubtful postulates Akulov gets the following results for magnetisation. If the areas between I_P-H_A curves are taken, not up to I_S as before but up to any arbitrary value I_P, the curves

$$\int_0^{I_P} H_A dI_P - \phi$$

where ϕ is the azimuth of H_A are derivable from the curve

$$\int_0^{I_S} H_A dI_P - \phi$$

by a mere change of scale. If I is maintained constant in magnitude by a suitable choice of H_A, the theory predicts that as the direction of I is allowed to vary $H_A I$ is the same function of the direction of I for all values of I. Experiments show that both these predictions are actually true. From this theory the value of the expression $H_A - (H_A)_0$ can also be evaluated, when H_A refers to the magnitude of the applied field in a random direction and $(H_A)_0$ to that applied in a principal direction of magnetisation corresponding to a given value of I_P. The predicted values are in good agreement with experimental values. It may be safely said that the theory of Akulov has proved to be a very successful one in dealing with all phenomena connected with ferromagnetism in magnetic fields of intensity greater than the coercive force. Under these conditions it is plausible to suppose that the whole lot of atomic magnets simultaneously orientate under the action of an increasing magnetic field constant in direction.

Becker's Theory.—An observation of E. Ising [26] that a cubic arrangement of dipoles has no magnetic stability when co-directed forms the background of Becker's theory [27]. In order to ensure this stability a deviation from cubic symmetry other than that due to the assignment of a common direction for the dipole axes has to be introduced. There are two possible ways in which this can be done:

(i) The assignment of suitable linear dimensions—with corresponding quadruple moment—to the unitary magnet. This procedure was adopted by Ewing and in a slightly modified form by Mahajani and Akulov.

(ii) The distortion of space lattice and the assumption that mechanical constraints are the chief causes of ferromagnetic stability and resulting hysteresis.

The later possibility has been explored by Becker, and the advantage of this postulate is that it permits a correlation of magnetic properties with mechanical strains and avoids the difficulties inherent in the work of Mahajani and Akulov regarding the hysteresis losses in single crystals and spontaneous magnetisation in zero field.

Becker postulates that the direction of I lies always in the plane determined by the direction of H_A and that of the strain determined by spontaneous magnetisation, I_0. The form and dimensions of the regions within which I_0 may be considered constant in direction remain undetermined. In regions containing but a few atoms each, the stable orientation of each atom is fixed mechanically by the distances and orientations of its nearest neighbours. A magnetisation curve representing correctly the behaviour of a metal crystal is derived by Becker on the plausible assumption that the local strains which fix in each region the direction of its initial magnetisation are larger in comparison with magneto-striction strains, so that the change in the elastic energy, due to rotating the magnets in any region, may be negligible. In each region the degree of strain, and the direction of magnetisation which the strain stabilises, together fix a critical field intensity, different for different directions of H_A, at which discontinuous changes in I_P take place for sufficiently wide ranges in H_A. In this manner Becker accounts for the coercive force, remanent magnetisation, a single Barkhausen discontinuity and a hysteresis energy loss per cycle for each region. An averaging over all the regions leads to the kind of hysteresis loop usually found in practice.

On this theory the maximum coercive force, explicable by purely elastic strains, is 140 gauss, which is in good accord with experimental facts. The coercive force depends directly upon the numerical factor which determines the magnitude and sign of the longitudinal magneto-striction effect. The wide variation of remanent magnetisation in different materials is attributed to the very large differences in the distribution function for the directions of I_0 in the unmagnetised specimen.

On Becker's theory it can be predicted that elastic stress on the specimen, as a whole, will alter the coercive force and the remanent magnetism. The direction of actual variation tallies with the predicted variation. It is interesting to note in this connection that Ewing and Evershed visualised the importance of elastic strain in changing the orientation of the magnets in their original models. They did not, however, postulate an initial strain which Becker introduced in his theory.

Besides these important theories a number of other theories have been put forward. Notable amongst them are the following.

Theory of Honda and Okubo.—The theory resembles that due to Ewing, with this difference that Honda and Okubo[28] make the atomic magnets much shorter than the least distance between atom centres and thus relatively increase the influence of non-adjacent atoms. Contrary to Ewing they also take into consideration the influence of neighbouring complexes with their elements in various orientations.

Dorfmann's Theory.—Dorfmann, Jaanus and Kikoin[10] have also tried to explain ferromagnetism as arising out of conduction electrons. Stoner[29] has criticised these theories and shown that an error in calculations arising out of a change in sign vitiates the quantitative agreement in favour of this theory. It finds qualitative support from the fact that magnetic properties and thermoelectric properties change rapidly at the same temperature. No direct relation between the two properties, however, is yet established and so the qualitative proof is also not very strong. The work of Smith and Dillinger[30] and of Fowler and Powel[31] deserves consideration, as they try to explain the facts with regard to the magnetisation of single ferromagnetic crystals by taking into account the magnetic interaction between each electron and the atom to which it belongs.

From what has been said above it would appear that a large amount of very interesting work has been stimulated by these theories. From a magnetochemical standpoint the interest still centres round the possible cause or causes for the ferromagnetism of the group, iron, cobalt, nickel and for such substances as the Heusler alloys and the compounds of the type manganese arsenide, manganese bismuthide, etc. A lead has been given by Slater and Stoner, but much still remains to be done. It is not improbable that many more ferromagnetic substances both organic and inorganic may be prepared when the theory becomes better understood. From a more practical standpoint the theories of ferromagnetism have still to explain quantitatively the phenomena of remanence, the loss of magnetisation on mechanical straining, the exact significance of the poles and the causes of their development. Some facts of chemical interest —for example, the possibility of the existence of the two types of manganese one of which exhibits ferromagnetism, and the case of the two borides of manganese (MnB and MnB_2) one of which (MnB) is intensely ferromagnetic—do not seem to have found a correct explanation.

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CHAPTER IX

MAGNETISM AND VALENCY

'To an organic chemist the valency of an atom in an organic molecule represents the number of "bonds" which tie this atom to other atoms.' This viewpoint has had signal success in the interpretation of molecular structure by the method of graphic formula. The achievement of these structural formulae in organic chemistry led to their adoption in inorganic chemistry, though not always with happy results. The artificial manner in which these structural formulae were employed led to a reaction which found its best expression in a publication entitled *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* by Werner. The growth of ideas advanced by Werner (1891) and the successful advent of the electrolytic dissociation theory directed the attention of chemists from structural formulae to finding an explanation of the chemical bond in terms of electrical force. Historically speaking, in 1812 Berzelius put forward the well-known 'Dualistic Theory'. Amongst those who added their weight to this theory were Davy and Avogadro. They regarded oxygen as the most electro-negative element, while Berzelius further assumed that every atom had two electrical poles—one positive and one negative—and as a rule unequally strong. Thus the atom possessed usually a predominating polarity. Chemical combination of the first order was considered to be due to the complete or partial neutralisation of opposite electricities. The combination of the second order was due to the electrical action between two particles of the first order having unneutralised residues of opposite electricities. Thus CaO for example, was supposed to possess a residual positive electrification and anhydride of sulphuric acid SO_3, a residual negative electrification. The combination between them resulted in complete neutrality and the formation of calcium sulphate. Berzelius' views were definitely controverted by Faraday's work on the laws of electrolysis which established beyond doubt that the chemical equivalents of elements are associated with equal quantities of electricity, thus disproving Berzelius' assumption of unequal charges. Dumas proved the inapplicability of this theory by showing that electronegative chlorine could replace electropositive hydrogen equivalent for equivalent without material change in the properties of an organic substance.

The views of Berzelius came again to the front in 1887 with the rise of Arrhenius' theory of electrolytic dissociation. It was recognised that atomic linkages are of two types, one ionisable and presumably due to electrostatic forces and the other non-ionisable and not explicable so easily. This distinction, however, was generally disregarded, but meanwhile new facts were accumulating which showed that two or more apparently saturated or electrically neutral molecules (as postulated by Berzelius) combined to form complex molecules of sufficient degree of stability. These compounds remained comparatively obscure till 1891 when Alfred Werner[1] brought them into prominence in his 'Co-ordination' theory.

1. WERNER'S THEORY OF VALENCY

When the binding capacity of an elementary atom, as defined by the theory of valency, appears exhausted Werner assumes that the atom can still link up with other molecules by a particular kind of affinity, named as the *Residual Affinity*, and build up more complex molecules. Werner, accordingly distinguishes two kinds of valency:

(*a*) *Chief or Primary Valency.*—It is the number which expresses how many atoms of hydrogen or of other atoms equivalent to hydrogen can unite with one atom of the element in question, being negative when in combination with electropositive atoms and positive when in combination with electronegative atoms.

(*b*) *Auxiliary, Secondary or Residual Valency.*—It represents those manifestations of chemical affinity which are able to bring about the stable union of molecules, and determines the number of molecules which can be directly attached to a central atom.

There is, however, a limit to the binding capacity of both primary and secondary valencies and the number which represents the joint effect of both the valencies is called the *Co-ordination Number.* It may be defined as the maximum number of atoms or groups of atoms non-ionisably but directly linked to the central atom. Usually the co-ordination number is constant, but it may vary with atomic volumes and temperatures. The intensity of force with which the co-ordinated atoms are attached to the central atom depends upon the valency of the co-ordinating atom, on the atomic volumes of the co-ordinated and co-ordinating atoms and on temperature.

Out of the atoms linked to the central atom by either primary or secondary valency only those dissociate in solution and give rise to electrically charged ions which owe their combination to a primary valency, the maximum number of such univalent ions with charge opposite to that of central atom being equal to the valency of the central atom, and the maximum number of those with the same charge as the central atom being equal to the difference between the co-ordination number and the valency of the central atom.

Werner further suggests that the number is decided by available space round the central atom rather than by affinity, that each co-ordinating atom occupies a corner of one of the five imaginary regular solids, and that the symmetry of the imaginary solid and the nature of the co-ordinated atom determine the isomeric forms of the co-ordination complex. When there is no centre, plane, or an alternating axis of symmetry, the isomeric forms are optically active, and exist in pairs. These, when in equal amounts, may give rise to racemic compounds which can be resolved into their components by any of the well-known methods.

From the above it may be concluded that the chemical evidence points to the existence of three types of linkages when atoms combine to form molecules:

(i) *Polar* linkages indicating the possibility of ionisation, for example, the oppositely charged ions of a salt.

(ii) *Non-polar* linkages distinguished by non-ionisability, for example, many organic compounds.

(iii) *Werner's Co-ordination* linkages capable of explaining the union of apparently saturated molecules.

The physicist has to develop his theory of molecular structure in the light of the above types of union between atoms and atoms.

2. ELECTRONIC THEORIES OF VALENCY: ABEGG'S RULE

When the electronic constitution of atoms was established, attempts were immediately directed to utilise the electrons for providing a satisfactory mechanism for chemical combination.

J. J. Thomson [2] was one of the first to suggest that the molecule is possibly held together by the electrostatic force as a result of the migration of an electron from one atom to another.

In 1904 Abegg [3] announced the rule which is called after him as 'Abegg's rule of 8'. The idea was naturally suggested to him by Mendeleef's relation between the valency of an element and its periodic group. Abegg believed that every element had both positive and negative valencies. The positive valency comes into play when an element combines, say, with a halogen and the negative valency when it combines, say, with hydrogen. Thus, according to Abegg, 'every element has both a positive and a negative maximum valency, the sum of which is always 8 and the former corresponds to the group number'. Thus as an example he gave the table:

Group . . .	1	2	3	4	5	6	7
Normal valency .	+1	+2	+3	±4	−3	−2	−1
Contra-valency .	(−7)	(−6)	(−5)		(+5)	(+6)	(+7)

Great significance to the views of Abegg was attached by Drude, whose comments contained the prophetic pronouncement:

'Abegg's positive valency number v, whether it is a normal or a contra-valency, signifies the number of loosely attached negative electrons in the atoms: his negative valency number v' means that the atom has the power of removing v' negative electrons from other atoms or at least of attaching them more firmly to itself. . . .' This view of Drude corresponds almost exactly to the ideas now prevalent. With the advent of the Rutherford model of atomic structure, the detailed physical theory of valency put forward by Stark [4] for non-polar compounds ceased to be of interest as it was based on Thomson's first concept of atom model. Not until the remarkable discovery of atomic numbers by Moseley did any definite advance take place in elucidating the relationship between valency and atomic structure.

3. Electronic Theory of Valency: Kossel and Lewis

The atomic numbers gave the number of electrons which constitute each atom and also indicated the peculiarly stable arrangement of the electrons in inert gases. The most daring and fruitful concept of valency and its relationship with atomic number was put forward simultaneously and independently in 1916 by Kossel[5] and G. N. Lewis[6], the former dealing with the polar compounds and the latter with non-polar organic compounds.

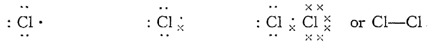
(*a*) *Polar Compounds.*—Kossel pointed out that a close study of the elements in relation to their atomic structure reveals the fact that the element just before an inert gas is always a strongly electro-negative and univalent halogen and that immediately following an equally strongly electro-positive and univalent alkali metal: that the element just before the halogen is negative and divalent, and that next following the alkali metal positive and divalent and so on: and that these facts could be simply explained by supposing that the inert gas had the highest degree of symmetry and stability regarding electronic configuration and that other atoms had a strong tendency either to give up electrons or to take up electrons in such a manner as 'to ape the structure of the nearest rare gas'. For example, in the series

	S	Cl	A	K	Ca
(Number of electrons)	16	17	18	19	20

since argon (A, 18) is the inactive rare gas, all elements in the series tend to take up that structure; sulphur by taking up two electrons, chlorine by taking up one, potassium by losing one and calcium by losing two electrons. This indicates vividly the tendency for the elements to form stable ions like S^{--}, Cl^{-}, K^{+}, Ca^{++}, and on combination to yield neutral salts like K_2S, KCl, $CaCl_2$, etc. The electro-negative part in the process of combination gains the necessary electrons from the electro-positive part, the ions in salt being held together by the electrostatic forces so produced.

On Kossel's theory the valency of an atom is the number of electrons it must gain (if electro-negative) or lose (if electro-positive) in order to have a total number which is capable of forming a stable inert gas configuration. The theory of Kossel is based upon atomic numbers without involving the acceptance of any particular atomic model. It explains in a satisfactory manner the connection between the valency of an element and its position in relation to the inert gases. As far as a particular group of compounds (namely the polar molecules) is concerned this theory accounts satisfactorily for all the facts including those of ionisation, spectroscopy and X-ray examination of crystals. It, however, fails to account for the non-ionised link or the non-polar compounds.

(*b*) *Non-polar Compounds.*—G. N. Lewis gave a solution of this problem. Like Kossel he also assumed that in chemical combination the tendency of the electrons is to redistribute themselves among the atoms and form stable and symmetric inert gas configurations, but he added to it the fundamental concept that it was possible for an electron to be shared between the atoms in a way such that it would add to the stability of both. As to how this happens is a question of fundamental interest for the physicist, but from the standpoint of the chemist it is enough to assume that such a sharing is possible in some manner. Thus chlorine which has seventeen electrons, one short of eighteen to complete the inert gas structure, can take up one electron, say, from a sodium atom to form a chloride ion with a negative charge. It can also complete its electronic shell by sharing an electron belonging for example to another chlorine atom, and if the second chlorine atom shares an electron from the first then each of the chlorine atoms is fully satisfied. The three states of the atom will be represented by



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\overset{\cdot}{\times} \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\overset{\cdot}{\times}\overset{\times\times}{\underset{\times\times}{\mathrm{Cl}}}\overset{\times}{\times} \text{ or } \mathrm{Cl}\text{—}\mathrm{Cl}$$

$$\mathrm{Cl}=(2)(8)(7) \qquad \mathrm{Cl}^{-}=(2)(8)(8) \qquad \text{—}\mathrm{Cl}=(2)(8)(6,\ 2)$$

(i) (ii) (iii)

4. ELECTROVALENCY AND COVALENCY—LANGMUIR

To distinguish the two types of linkages between polar and non-polar compounds, Langmuir[7] introduced the terms 'electrovalency' and 'covalency', which have been universally adopted. The electrovalency of Kossel for a negative element is equal to the number of electrons that it needs to make up a stable configuration. According to Lewis' theory it should gain an electron for each covalency that it forms. Thus the number of covalencies must be equal to this defect and the same applies to electrovalency. In the case of a positive element the number of electrons, in excess of the stable inert configuration represent its electrovalency and correspondingly on the Lewis theory (since an atom in forming a covalent linkage not only takes an electron from the other atom but also contributes one of its own for the sake of stability) the number of covalent links are numerically equal to the electrovalent links.

According to the Kossel-Lewis theories, it has been possible to arrive at the following mechanism of the three types of linkages one meets with in chemistry:

(i) *Polar or ionisable linkage*. This is due to the transference of electrons from one atom to another and termed by Langmuir as *Electrovalency*.

(ii) *Non-polar or non-ionisable linkage*. This is due to the sharing of electrons two to each link between the atoms and termed as *Covalency*. There are at least two ways in which covalent linkages can be formed:

(*a*) Both electrons may be contributed by the same atom in which case they are termed as 'Co-ordinate covalencies'. In this case the numerical value for covalency is independent of the periodic group to which the atom is assigned.

(*b*) One electron may be contributed by each of the atoms, in which case the term 'normal covalencies' is used and the numerical value of this is limited by the periodic group of the atom.

5. VALENCY AND AFFINITY

The above résumé of the present position of the theory of valency raises the important question regarding the source of chemical affinity. The electrochemical theory has been shown by Lewis and his school to be entirely incapable of giving a satisfactory answer to this question. While electrostatic forces evidently have an important rôle in the process of ionisation and possibly also in reactions which are of the ionic type, these forces cannot be proved to be responsible entirely for the fundamental arrangement of electrons within the molecule nor for the formation of bonds which bind the molecules.

The incompetency of simple electrostatic forces to account for the characteristics of chemical combination can be further realised from a simple comparison between an atom of argon with a positive nuclear charge of eighteen, surrounded by eighteen electrons, and an atom of potassium having a positive nuclear charge of nineteen, surrounded by nineteen electrons. It might be expected that the removal of an electron will be about equally difficult from each of these atoms. We find, on the contrary, that while it takes about four volts to ionise a potassium atom, it requires about fifteen volts to ionise the argon atom.

Also helium with a nuclear charge of +2 requires twenty-five volts to ionise, while lithium with a nuclear charge of +3 requires only five volts. In order to account for some of these phenomena various magnetochemical theories have been proposed from time to time. Reference may be made here to the views put forward by Ramsay[8], Parson[9], G. N. Lewis[10], Dorfmann[11], Stoner[12], Wilsdon[13], and many others.

I. *Valency and Magnetic Properties of Substances*

6. ELECTRON PAIR THEORY OF G. N. LEWIS

G. N. Lewis[10] considers the pairing of electrons, which certainly is one of the most important factors of chemical combination, as nothing else but some sort of conjugation of two elementary magnets of such character as to neutralise mutually their magnetic moment. According to him the first law of chemical affinity is that electrons in an atom or a molecule tend to pair with one another in such a manner as to eliminate magnetic moment. The highest degree of chemical unsaturation is therefore represented by an odd molecule (molecule having odd number of electrons) which is characterised by the tendency to orient itself in such a manner as to reduce the total unsaturation to a minimum. Thus the odd molecule enters into chemical combination most readily even with molecules which are least unsaturated. It is in this connection that the possibility of magnetism being one of the factors in valency seems to suggest itself.

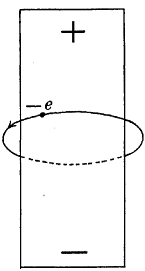


FIG. 41A

It is abundantly clear from above that the odd electron must play some part in valency problems. E. H. Williams[14] suggested a simple method of joining two electronic orbits, a diagrammatic representation of which is shown in Fig. 41, A and B. A revolving electron may be considered equivalent to a magnet with polarity, as shown in Fig. 41A. Two such electromagnets approaching each other, as in Fig. 41B, will be attracted with a magnetic force depending on some inverse function of the distance between them. There is nothing to prevent the electronic orbits overlapping each other and thus making the distance between effective poles very small. If the atom contains an even number of electrons it is possible, on the magnetochemical view, to assume that they would pair off and thus constitute a substance which will have no magnetic moment and will exhibit diamagnetism. There are, however, many substances of even atomic number which are not diamagnetic, for example, iron, nickel and oxygen. The real test of the magnetochemical theory, however, is not this. In order to test it rigidly we should examine the case of odd molecules. As the tendency of electrons is to occur in symmetrical groups or in pairs, it is difficult to obtain many substances of odd molecular number. Careful investigations on this point have been carried out by E. H. Williams, Taylor[15] and by Shaffer and Taylor[16]. The following table sums up the conclusions arrived at by E. H. Williams.

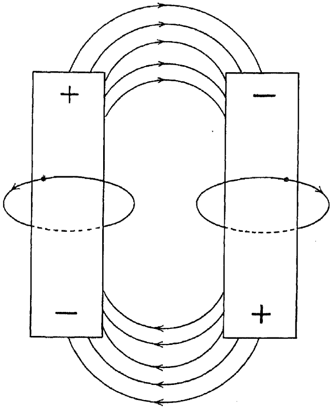


FIG. 41B

A glance at the table shows at once the interesting fact that all odd molecules are paramagnetic. The single exception of

TABLE I

MAGNETIC SUSCEPTIBILITIES OF ODD AND EVEN MOLECULES

Substance	$\chi \times 10^6$
CuO (odd)	$+1.35$
Cu_2O (even)	-0.34
$CuCl_2$ (odd)	$+8.77$
CuCl (even)	-0.41
$CuBr_2$ (odd)	$+2.71$
CuBr (even)	-0.34
BiO_2 (odd)	$+1.55$
Bi_2O_3 (even)	-0.26
PbO (even)	-0.19
PbO_2 (even)	-0.20
SnO (even)	-0.14
SnO_2 (even)	-0.14
MnO (odd)	$+66.3$
Mn_2O_3 (even)	$+63.1$
CoO (odd) (H = 1190 c.g.s. units)	$+630.0$
Co_2O_3 (even)	$+27.5$
AgO (odd)	-0.14
Ag_2O (even)	-0.58

AgO* and the curious behaviour of some even molecules of manganese and cobalt find a suitable explanation which has been indicated in the next paragraph.

The more accurate work of Soné[17] also shows clearly that while N_2, N_2O, N_2O_3 liquid, N_2O_4 liquid, N_2O_5 solid are all diamagnetic the two odd molecules NO_2 and NO in the family are paramagnetic. 'When we realise that the essential difference between two molecules of NO_2 and one molecule of N_2O_4 is that the two odd electrons or electronic orbits of the former have been clamped together to provide the chemical bond in the latter, we have as striking an illustration of the significance of pair formation as could be desired.' Further, N. W. Taylor has shown that chlorine dioxide, thallium dissolved in mercury, an organic free radical (α-naphthyl-diphenylmethyl) and a solution of sodium in liquid ammonia show definite paramagnetism.

From the data available on the subject, one can safely conclude that the magnetochemical theory is supported by the fact that all odd molecules are paramagnetic. The oxides of manganese and cobalt afford an interesting study. The atomic number of manganese is 25 and is very close to the ferromagnetic group iron, cobalt, nickel with atomic numbers 26, 27, 28. E. H. Williams' measurements show that the two oxides of manganese, namely MnO (odd) and Mn_2O_3 (even) are paramagnetic but the value for the oxide (even) was always less than that for the odd molecule. There is thus ample evidence of some pairing of electrons when the manganese atom with its odd electron is added to MnO. The oxide of cobalt which is an odd molecule (CoO) is not only paramagnetic but shows decided signs of ferromagnetism. The oxide Co_2O_3 which is an even molecule is much less paramagnetic than the odd oxide. The diamagnetism of AgO, according to Williams, is probably due to its composition being more truly represented by the formula Ag_2O_2, which shows it to be an even molecule.

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* Chemically speaking, the existence of AgO is not recognised.

Shaffer and Taylor[16] studied the influence of various diamagnetic substances such as hydrogen ion, chloride ion, bromide ion, cyanide ion, ammonia and methyl-amine on the paramagnetic susceptibilities of aqueous solutions of nickelous chloride and bromide, cupric chloride and cupric bromide. They found that there was a definite reduction of paramagnetism in all cases where complex ions of considerable stability were known to form. From this they conclude that the chemical bonds are partly or wholly magnetic in character. These results also indicate the fact that the bonds are formed by the same electrons which give rise to magnetic properties. The hypothesis of G. N. Lewis which suggests that two electron orbits in forming a chemical bond may pair in such a way that their magnetic fields may partly or wholly compensate seems to be capable of explaining the above facts.

7. THE ELECTRON-PAIR BOND ON QUANTUM MECHANICS

The empirical rules of G. N. Lewis regarding the sharing of electrons have acquired a theoretical justification on the principles of wave mechanics applied to molecular structure. The main credit for clarifying this subject and for interpreting the mechanism of bond formation goes to Burrau[17a], Heisenberg[18], Heitler and London[19], and Linus Pauling[20].

(*a*) *Burrau's Proof of the Structure of* H_2^+.—Burrau investigated the problem of the hydrogen molecule ion H_2^+. Its existence was early established in the positive ray experiments and the molecule ion was found to give a characteristic band spectra. The average life of an excited atom associated with an atom emitting radiation is of the order of 10^{-8} seconds, while the average life of this molecule is considerably longer, being of the order of 2×10^{-2} seconds. This molecule has been shown to consist of two hydrogen nuclei and one electron. A pictorial way of looking at it is to regard the electron to be bound by one nucleus to form a normal hydrogen atom and to let the other nucleus be brought up slowly to a small distance from the first. Heisenberg and Dirac discovered that for a system like this the perturbations of the electron by the second nucleus can lead to an oscillation of the electron between orbits around the two nuclei. As a result of this oscillation a new term has to be introduced into the expression which represents the total negative energy of the system and which is equivalent to the work required to break up the system. This quantity is of great significance as it is a good and accurate measure of the stability of the system. The new energy term introduced as a result of this oscillation may have a positive or a negative sign depending upon the quantum numbers which define the energy levels of the oscillating electron between the two nuclei, and thus the re-

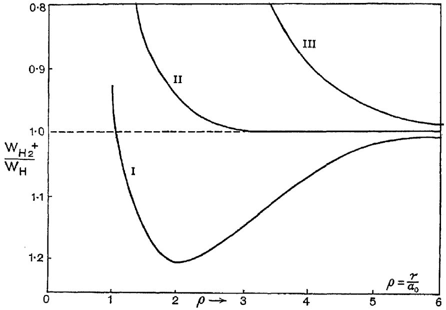

FIG. 42.—Curve I, showing the total energy for the normal hydrogen molecule ion as calculated by Burrau. Curve II, in which the potential function is obtained neglecting the resonance phenomenon. Curve III, showing the potential function of the antisymmetrical eigenfunction.

sonance or interchange energy may either decrease or increase the stability of the system. The wave equations for this system have been worked out by Burrau, who has also calculated the value of the negative energy of the systems for different distances r between the two nuclei.

For the sake of facilitating the discussion of Burrau results, we shall consider them in Fig. 42, in which the ratio of $W_{H_2}{}^+/W_H$ is plotted against $\rho(=r/a_0)$. In curve I, for ρ greater than 1·1 units, the interchange energy has a positive sign which denotes an increase in the stability of the system, $W_{H_2}{}^+$ becoming greater than W_H. At $\rho=2·0$ or $r=1·06$ A° the stability is greatest and corresponds to the formation of a stable molecule. Curve II indicates that the ratio $W_{H_2}{}^+/W_H$ is always less than unity and a stable molecule cannot be formed, as their values indicate clearly that the system is less stable than a separate hydrogen atom and a hydrogen nucleus for all values of r. In curve III the energy $W_{H_2}{}^+$ is always less than W_H and the hydrogen atom does not unite or get attracted to the impinging proton. From these considerations it is clear that the possibility of existence and the stability of a molecule is dependent upon the interchange energy, and it is this energy which gives rise to a non-polar bond.

(*b*) *Structure of* H_2 (*Heitler-London*).—The problem of the structure of hydrogen molecule has been theoretically discussed by Heitler and London, on the same lines as that of the $H_2{}^+$.

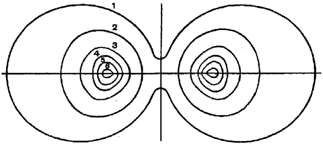

FIG. 43A.—Contours representing the electron distribution for two hydrogen atoms in elastic collision (antisymmetrical configuration). (London.)

In this case two electrons oscillate between the two nuclei. The statistical average charge distribution in H_2 molecule can be calculated directly from the quantum postulates and is shown in Figs. 43, A and B. The statistical charge density is represented by the contour lines, the density being larger where the lines are closer together and smaller where they are farther apart, the densest region being nearer the nuclei. The mathematical analysis shows that there are two solutions of the Schrödinger wave equation corresponding to the interaction between two hydrogen atoms. In one case shown in Fig. 43A the forces exerted on the nuclei are entirely of the nature of a repulsion, which means that it is not always necessary that the two atoms of hydrogen in contact should form a molecule. In the other solution (Fig. 43B) there is attraction as well as repulsion, and this is what makes possible the formation of a stable molecule.

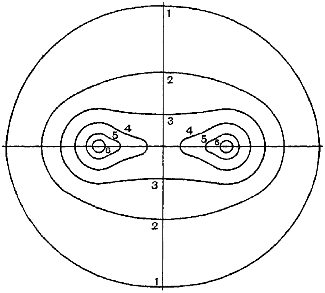

FIG. 43B.—Electron distribution for two hydrogen atoms in the process of forming a molecule. (London.)

(*c*) *London and Heitler Spin Theory of Valency.*—London and Heitler[19] noticed that in hydrogen a valency bond is formed when two unpaired electrons become paired and both go into the same kind of orbit, or in other words become symmetrically related. London and Heitler generalised these observations in their well-known theory of valency, according to which the establishment of a symmetrical relation between two electrons originally belonging to two separate atoms is a characteristic feature of the valency bonds in general. On this theory the valency V of an atom is then supposed to be equal to the number of unpaired electrons. Since for each unpaired electron $s=1/2$, and since all these unpaired electrons stand parallel to each other, they will give a resultant spin quantum number equal to V/2.

Thus $V=2S$. But as the term multiplicity is equal to $2S+1$ (cf. Chapter V, Section 12), the valency may be defined as one unit smaller than the multiplicity of the term corresponding to the normal atomic state. As a consequence of the Pauli principle, when unpaired electrons become paired or get symmetrically related, for example when a molecule is formed, their spins pair off as well. Thus if two atoms, each having the same number n of unpaired electrons and spin $S=n/2$, unite so that all the electrons thereby become paired the molecule has zero resultant spin and is diamagnetic.

The quantum mechanical theory thus provides a formal justification of the rules of G. N. Lewis.

8. THE NATURE OF THE CHEMICAL BOND ON QUANTUM MECHANICS—LINUS PAULING

From considerations of quantum mechanics Linus Pauling[20] has been able to confirm the empirical rules of G. N. Lewis, and to extend them to cover many other significant facts of chemistry. This treatment provides formulation of a set of rules regarding the relative strength of bonds, the angles between the bonds, free rotation or absence of free rotation about the axes of bonds, correlation between the quantum numbers of bonding electrons and the number and spatial configuration of the bonds. A complete theory of the magnetic moments of molecules and complex ions based upon quantum mechanics has also been developed.

Before Pauling came in the field, Heitler and London[19], Sugiura[21] and Wang[22], in discussing the wave equation for the hydrogen molecule, had come to the following conclusions:

(*a*) That two normal hydrogen atoms can interact in either of two ways, one of which gives rise to repulsion with no molecule formation and the other to attraction and the formation of a stable molecule.

(*b*) The characteristic resonance phenomenon which produces the stable bond in hydrogen is always through the interaction of an unpaired electron in each of the two atoms.

(*c*) The spins of the electrons are opposed when the bond is formed, so that the bonds cannot contribute to the paramagnetic susceptibility of the substance.

(*d*) Two electrons which form a shared pair cannot take part in forming additional pairs.

Besides the above, L. Pauling has added the following three rules which, according to him, are justified by the qualitative consideration of the factors influencing bond eigenfunction:

(*e*) The main resonance terms for a single electron-pair bond are those involving one eigenfunction from each atom.

(*f*) Of two eigenfunctions with the same dependence on r, the one with the larger value in the bond direction will give rise to the stronger bond and for a given eigenfunction the bond will tend to be formed in the direction with the largest value of the eigenfunction.

(*g*) Of two eigenfunctions with the same dependence on θ and ϕ, the one with the smaller mean value of r, that is the one corresponding to the lower energy level for the atoms, will give rise to the stronger bond.

Here the eigenfunctions referred to are those for an electron in atom, and r, θ and ϕ are polar co-ordinates of the electron, the nucleus being at the origin of the co-ordinate system.

Further, according to Pauling the type of bond formed by an atom is dependent upon the ratio of bond energy to the energy of penetration of the core (s-p separation). When this ratio is small, the bond eigenfunctions are p eigenfunctions, giving rise to bonds at right angles to one another. When this ratio is large new eigenfunctions specially suited to bond formation can be adopted. From s and p eigenfunctions the best bond eigenfunctions which can be made are four equivalent tetrahedral eigenfunctions, giving bonds directed towards the corners of a regular tetrahedron. These account for the tetrahedral atom so successfully employed by the chemist to explain the structural facts particularly of organic molecules. They also satisfactorily and in a perfectly natural way explain the possibility of free rotation about a single bond and not about a double bond. The case of bivalent nickel, palladium and platinum is easily accounted for by assigning to them a single d eigenfunction with s and p. This would give rise, on Pauling's treatment, to four strong bonds lying on a plane and directed towards the corners of a square—a very good representation of the behaviour of the bivalent platinum, etc. The d eigenfunctions with s and p may give rise to as many as nine eigenfunctions, six of which are equivalent and constitute the six octahedral eigenfunctions characteristic of complexes formed by the elements of the transition group. Besides these remarkable results, what is most important to us is the relationship which Pauling has shown to exist between the magnetic moments of molecules and the unpaired electrons. This aspect of the Pauling theory has been treated in the next sections of this chapter along with the historical development of the theoretical interpretations of the magnetic properties of simple and complex molecules. It would not be out of place to mention here that, although it is customary to treat the electron pair as the normal unit bond, the view that a special kind of bond known as the 'single-electron bond' may occur in some molecules has been employed by several workers, notably by Sugden[23], in explaining higher valencies. This makes the singlet linkage a phenomenon of a very frequent and general occurrence. The magnetic investigations of Angus and Farquharson[24] and of Bhatnagar and Lahiri[25] show that the singlet linkages do not seem to exist in the case of Be and Te compounds (cf. Chapter XIV, Section 7).

While Sugden's views have not found general acceptance, Pauling[26] has recently shown the existence of single-electron bonds in rare cases, particularly in H_2^+. He has also introduced the concept of a 'three-electron bond' in certain molecules such as He_2^+, NO and O_2. According to Mulliken[27], all such special concepts can be reduced to terms of bonding and anti-bonding electrons.* The one-electron bond is a single bonding electron, the electron-pair bond is two bonding electrons symmetrically related, while the three-electron bond consists of a pair of bonding electrons plus one anti-bonding electron.

Before discussing further the applications of wave-mechanical theories in connection with molecules and their magnetic properties it is desirable to consider in historical sequence the contributions made by G. N. Lewis, Sidgwick and others which had prepared the way for the modern theories. Although the older concepts have been largely superseded, the reason for a more or less fuller treatment of their work is that they still form a good objective background for the chemist and explain a large number of facts satisfactorily.

II. *Valency and Magnetic Properties of Molecules and Ions*

9. RESIDUAL AFFINITY

In his remarkable book on *Valence and the Structure of*

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* A bonding electron is defined as one which has large positive 'bonding power' (B.P.), an anti-bonding electron has large negative B.P., while a non-bonding electron has very small B.P.

Atoms and Molecules G. N. Lewis introduces the idea of residual affinity in the following words:

'When all the electrons in a molecule are paired, even if we assume that the magnetic moment of a bonding pair and of every other electron pair is exactly zero, it would be neither necessary nor desirable to assume that the magnetic fields of the paired electrons completely neutralise one another. In other words, we may assume the complete disappearance of magnetic moment (although this has not yet been definitely proved), and at the same time we may assume a residual magnetic field emanating from the electron pair. This stray field we shall now consider to be equivalent to what has been called residual affinity, and to be responsible for that condition which we have spoken of as a condition of unsaturation. This residual affinity is therefore of a very different kind from that which would be due to electric polarisation, where it would be necessary to assume two kinds of field, one emanating from a positive and one from a negative charge.

'The several pairs of electrons in an atom may arrange themselves in such an orientation as to neutralise still further their residual fields. The second fundamental principle of chemical affinity may therefore be stated as follows: *Every atom, except that of hydrogen or helium, has the smallest external magnetic field, and is therefore in a condition of maximum stability, when it possesses in its outer shell four pairs of electrons situated at the corners of a regular tetrahedron.* The condition of saturation accompanying such an arrangement is best exemplified by the atoms of the argon type. The noble gases in their diamagnetic behaviour and in their chemical inertness show a nearer approach to complete saturation, or lack of residual affinity, than any other known substances.'

10. UNSATURATION FROM THE MAGNETOCHEMICAL STANDPOINT

If a stable and symmetrical structure undergoes distortion in any way the disturbance results in an increase in the residual magnetic field and this distortion travels and affects the neighbouring molecules in such a manner that the total resultant unsaturation is reduced to a minimum. 'All such distortions of the molecule, with the accompanying increase in residual magnetism, may be considered to be due to the change in the relative position or orientation of the several pairs or to the partial "opening up" of a single pair, and probably either of these effects ordinarily accompanies the other.'

Leaving aside the odd molecules, in organic chemistry those molecules to which we ascribe multiple bonds are more unsaturated, and more particularly those which possess double bonds. The chemical and the magnetic properties of molecules with double bonds show a higher degree of unsaturation, as is evident from the work of Pascal, who showed that in the case of substances with a double bond between carbon and carbon, carbon and nitrogen, nitrogen and nitrogen or carbon and oxygen the magnetic susceptibilities cannot be calculated from the addition of atomic susceptibilities and the double bond behaves as if a paramagnetic carrier was present in the compound (cf. Chapter IV, Section 8).

As compared with the double bond, a triple bond produces comparatively smaller diminution in diamagnetism. This also is borne out by the investigations of Pascal on compounds containing triple bonds between carbon and nitrogen and carbon and carbon, as well as by the diamagnetism of the nitrogen molecule itself. While the interesting parallelism between diamagnetism and chemical saturation is a recognised fact, it is not possible to give an exact quantitative interpretation of the magnetic properties of molecules on account of a lack of knowledge of the arrangements of shared and unshared electrons in molecules and the inadequacies of the theories of diamagnetism themselves.

11. EFFECTIVE ATOMIC NUMBER AND THE SIDGWICK RULES

The first important thing is to find a method by which it may be possible to determine the number of unshared electrons in a molecule. This is the so-called Effective Atomic Number of Sidgwick[28], denoted by E.A.N. or Z. The simple rules for determining this are as follows:

(i) For each covalency due to the attachment of a univalent radical we add one.

(ii) *(a)* For each co-ordinate valency when the atom attaches itself to a complete molecule and the former acts as acceptor we add two; *(b)* when it acts as donor no change is made.

(iii) If the resulting complex is an ion, we add the value of its negative electrovalency or subtract that of its positive electrovalency.

We shall illustrate these rules with examples and try to make their application clear.

Atoms in Various States of Combination	Effective Atomic Number (E.A.N.) or Z
C in CH_4	$6+4 = 10_4$
B in $K(BF_4)$	$5+4+1 = 10_4$
N in NH_3	$7+3 = 10_3$
N in $(NH_4)Cl$	$7+4-1 = 10_4$
Co in $(Co(NH_3)_5Cl)(NO_3)_2$	$27-2+1+(5 \times 2) = 36_6$

The subscript under the effective atomic number gives the number of covalent links of the atoms in the state of combination and denotes the number of pairs of shared electrons. The number of unshared electrons is the effective atomic number minus twice the covalency. Thus, in the last case in the above table, 36_6 denotes that the number of unshared electrons is $36-(2 \times 6)=24$.

In this way we can find out how many effective electrons the atom has in the compound and how many of them are shared.

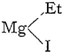
The next question is to find the distribution of these electrons into groups in accordance with laws which Bohr and others have shown to obtain in isolated atoms. Here we are treading on rather uncertain ground. The safe procedure is to follow the methods adopted by the physicists in fixing molecular states from spectroscopy.

Accordingly it can be safely assumed that in molecules the sharing of the valency electrons makes no difference to the distribution of the unshared ones so far as the lowest quantum groups are concerned. These unshared electrons of the molecules are assumed to fill in the quantum groups in precisely the same manner as in isolated atoms. Thus the total number of electrons as grouped in molecules can be represented on the same principles as in the case of atoms.

It is conventional to distinguish the shared from the unshared electrons. This may be done by underlining the former, but as they always occur in pairs it is convenient to write them as two equal numbers and underline them, for example:

Sn in $SnCl_4$ . . $50+4=54_4=(2)(8)(18)(18)\ \underline{4},\ \underline{4}$

In in $InCl_3$ . . $49+3=52_3=(2)(8)(18)(18)\ 3,\ 3$

Mg in  . $12+2=14_2=(2)(8)\ \underline{2},\ \underline{2}$

$Mg\langle^{Et}_{I}$

Pb in $Pb(C_6H_5)_4$. $82+4=86_6=(2)(8)(18)(32)(18)\ \underline{4},\ \underline{4}$

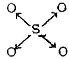
Pt in $K_2(PtCl_6)$. $78+6+2=86_6=(2)(8)(18)(32)(14)\ \underline{6},\ \underline{6}$

Mg^{++} . . $12-2=10_0=(2)(8)$

Mg in CH_3—Mg—I . $12+2=14_2=(2)(8)\ \underline{2},\ \underline{2}$

$(S)^{--}$ . . $16+2=18_0=(2)(8)(8)$

P in $(PH_4)I$ . . $15+4-1=18_4=(2)(8)\ \underline{4},\ \underline{4}$

S in  . . $16+2=18_4=(2)(8)\ 4,\ 4$

Extensive use has been made of Sidgwick's interpretation of electronic arrangement in atoms and molecules to elucidate their physico-chemical behaviour. This arrangement at least qualitatively accounts for the magnetic properties of a large number of molecules, ions and complex compounds, which are treated in the sections that follow.

As far as the monoatomic ions are concerned, the relation of their magnetic properties to electronic structure is at least qualitatively clear on the older concepts. All ions which are composed of complete electronic groups, for example K^+ 18,

TABLE II

EFFECTIVE ATOMIC NUMBERS AND MAGNETIC PROPERTIES OF IONS

Atomic Number of the Element	Ion	Effective Atomic Number of Ion	Magnetic Character
21	Sc^{+++}	18 (2)(8)(8)	Diamagnetic
29	Cu^{+}	28 (2)(8)(18)	,,
29	Cu^{++}	27 (2)(8)(17)	Paramagnetic
57	La^{+++}	54 (2)(8)(18)(18)(8)	Diamagnetic
58	Ce^{++++}	54 (2)(8)(18)(18)(8)	,,
71	Lu^{+++}	68 (2)(8)(18)(32)(8)	,,
72	Hf^{++++}	68 (2)(8)(18)(32)(8)	,,

Ca^{++} 18, F^- 10, I^- 54, Cl^- 18, etc., having inert gas configuration and Cu^+ 28, Zn^{++} 28, Cd^{++} 46, etc., with E.A.N. eight units less than the nearest inert gas configuration, are diamagnetic. Paramagnetism is only found among the ions of the transitional elements and the rare earth metals and their ions which all contain incomplete electronic groups. For the rare earth metals from lanthanum (57) to lutecium (71) and for the elements of the first long period from scandium (21) to copper (29) this conclusion is completely established. A few examples are given in Table II.

The ions of the intervening elements (59) to (70), in which the N shell contains more than eighteen and less than thirty-two electrons, are paramagnetic.

The following table sums up the results of a large number of workers on ions and makes it clear that the magnetic moment of the ions primarily depends on the number of electrons and not on the nuclear charge.

TABLE III

MAGNETIC MOMENTS OF IONS OF THE IRON GROUP

Effective Atomic Number	Electrons in the M Shell	Ions	Weiss Magneton, p	Effective Bohr Magneton, μ_B
18	8	K^+, Ca^{++}, Sc^{+++}, Ti^{++++}	0	0
19	9	Ti^{+++}	9	1·82
20	10	..	..	..
21	11	V^{++}	9	1·82
		Cr^{+++}	19	3·83
		Mn^{++++}	20	4·04
22	12	Cr^{++}	24	4·94
		Mn^{+++}	25	5·05
23	13	Mn^{++}	29	5·86
		Fe^{+++}	29	5·86
24	14	Fe^{++}	26	5·25
25	15	Co^{++}	25	5·05
26	16	Ni^{++}	16	3·23
27	17	Cu^{++}	9	1·82
28	18	Cu^+Zn^{++}	0	0

Thus it is seen that the magnetic moments for Cr^{+++} and Mn^{++++}, for Mn^{++} and Fe^{+++}, and for Cr^{++} and Mn^{+++} are more or less the same. Also, as the number of electrons increases from eighteen to twenty-three, the magnetic moment rises by almost five Bohr magnetons for the first five electrons added to the original eight in the M shell and falls again by similar amounts for the subsequent five electrons. According to the older theory the magnetic moments should all be integral Bohr units, and further, the addition of an electron should result in changing the moment by one whole Bohr unit. That this is far from being the case will be easily seen from the table in which the values on the Bohr units are all fractional.

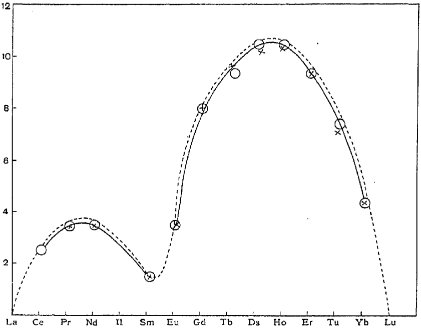


FIG. 44.—Effective magnetic moments of rare earth ions. The broken curve represents the theoretical Hund-Van Vleck Curve.

⊙=mean values of Cabrera and St. Meyer. =latest values of Cabrera and Duperier.

The discrepancies were sought to be explained in an artificial manner by emphasising the complexities of the structure of these ions.

The other paramagnetic group of rare earth metals is of fundamental importance from the magnetochemical point of view. The immense difficulties involved in the purification of the rare earth compounds made the task of the investigator very troublesome, and a good deal of work was provoked by the earlier discrepancies in the experimental values due to the presence of impurities. In Table IV and Fig. 44 are given the mean values from the data of Cabrera[29] and Stefan Meyer[30]. The former studied the crystalline hydrated sulphates and the latter the sulphates and some of the oxides. These two independent results compare favourably with each other.

TABLE IV

MAGNETIC MOMENTS FOR IONS OF THE RARE EARTH ELEMENTS *

Ion	Effective Atomic Number	Electrons in the N shell	Weiss Magneton, p	Effective Bohr Magneton, μ_B
La^{+++}	54	18	0	0
Ce^{++++}			0·8	0·16
Ce^{+++}	55	19	11·4	2·30
Pr^{++++}			13·8	2·79
Pr^{+++}	56	20	17·6	3·55
Nd^{+++}	57	21	17·8	3·59
Il^{+++}	58	22	..	..
Sm^{+++}	59	23	7·5	1·51
Eu^{+++}	60	24	18·0	3·63
Gd^{+++}	61	25	40·0	8·08
Tb^{+++}	62	26	46·0	9·29
Ds^{+++}	63	27	52·6	10·62
Ho^{+++}	64	28	52·0	10·50
Er^{+++}	65	29	46·9	9·47
Tu^{+++}	66	30	36·5	7·37
Yb^{+++}	67	31	22·2	4·48
Lu^{+++}	68	32	0	0

* For more recent values see Table IV, Chapter VII.

It is thus evident that the moments are zero for ions with fifty-four and sixty-eight electrons. These ions have the completed groups in N shell of eighteen and thirty-two electrons and are thus capable of forming diamagnetic inert gas configurations.

Here again the departure from the integral rule for Bohr units is quite prominent. A satisfactory explanation of the paramagnetism of the rare earth ions on the modern concepts has already been discussed in Chapter VII, Section 13.

12. RECENT THEORIES OF THE MAGNETIC PROPERTIES OF MOLECULES AND IONS

The credit for making the subject amenable to a quantitative treatment goes largely to Hund[31], Van Vleck[32], Pauling[20], Bose[33] and Stoner[34]. Reference has already been made to the treatment of the rare earth ions on the older theory in the last section. The significance of the new theory is borne out most satisfactorily by the very exact concordance with which the results for rare earths can be reproduced by the Hund formula

$$\mu^2{}_J = g^2 J(J+1)$$

where μ_J is calculated from the relation*

$$\mu_{\text{eff}} = \sqrt{\frac{3\chi_M kT}{N\beta^2}} = 2{\cdot}839\sqrt{\chi_M T}$$

or its modification—the Van Vleck-Frank formula—

$$\chi_M = \frac{N\beta^2}{3kT} g^2 J(J+1) + N\alpha$$

A full treatment of the subject has already been given in Chapter VII, Section 13. While these formulae of Hund and Van Vleck have been so successful in dealing with the rare earth salts and ions, they fail completely to account for other molecules and ions, and particularly for those of the iron group. It would appear at first sight that because the multiplet widths are more precisely known for the free ions of the iron group the formulae would give better agreement for this group. Such, however, is not the case. The history of the clearing up of this anomaly is rather interesting.

In 1924, a year before Hund put forward his treatment of the rare earth ions, Sommerfeld [35] noticed that by substituting in the equation $\mu_S = 2\sqrt{S(S+1)}$, the values for S equal to 0, 1/2, 1, 3/2, 2, 5/2, 2, 3/2, 1, 1/2 and 0 the calculated magnetic moments of K^+ and Ca^{++}, Ca^+ (spectroscopic), Ca (spectroscopic), Cr^{+++}, Cr^{++}, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++} and Cu^+ respectively agreed with the observed values. Bose [33] in 1927 introduced the tacit assumption that only the spin moment S contributes to the magnetic moment in these cases. Stoner in 1929 gave theoretical reasons justifying this procedure.

The essential difference between the rare earth ions and the iron group has been treated before. It has been shown that the incomplete $4f$ sub-shell responsible for paramagnetic properties in rare earths lies buried under an inert gas configuration of eight electrons of higher total quantum number. In this case, therefore, there cannot be any possibility of an interaction between the solvent molecules and the electrons responsible for paramagnetism. In the iron group the incomplete sub-shell lies just under the valence electrons, and as these are removed due to ionisation, the incomplete group will be, so to say, 'laid bare' to the action of the solvent molecules. According to Van Vleck if the L and S coupling is not strong enough to give a resultant J (Russell-Saunders coupling) the two vectors should be considered separately. Since the symmetry of the charge distribution of an ion depends on the orbital moment L, Stoner considers that the definite arrangement of ions relatively to each other in a crystal suggests the possibility of a strong l-interaction, leaving at the same time the spin moment comparatively free. This leads to the argument that in such a case of strong l-interaction the magnetic field will only affect the spin moments giving for the magnetic moment the value $\mu_S{}^2=4S(S+1)$. When the l-interaction is weak, L and S will be coupled more strongly and the moment should be given by the equation $\mu_J{}^2=g^2J(J+1)$ corresponding to $\Delta\nu\rightarrow\infty$ or $\Delta\nu=k\mathrm{T}$, as the case may be.

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* According to Hund's formula μ_{eff} is a function of temperature if the Curie law $\chi T = \text{const.}$ is not obeyed. Even if the Curie law is obeyed μ_{eff} will still be a function of temperature if the term $N\alpha$ of the Van Vleck-Frank formula is not negligible.

We might re-examine the iron group on all the various possibilities open to us. In discussing the Van Vleck treatment of paramagnetism we considered three cases corresponding to the observed term multiplicities and differentiated according to (i) $\Delta\nu\rightarrow 0$, (ii) $\Delta\nu\rightarrow\infty$, (iii) $\Delta\nu=k\mathrm{T}$ ($\Delta\nu$ being actual observed value). To this we add the fourth possibility of 'spin only' (μ_S) according to Bose-Stoner formula (Chapter VII, Section 13*b*) In Table V we have put the calculations on all the above considerations alongside the observed magnetic moments.

A glance at the table reveals at once the fact that the agreement is much better for μ_S than for μ_J ($\Delta\nu$ actual). The agreement, however, is not perfect. For example, the calculated value of μ_S for V^{+++} is larger than the observed value, while reverse is the case with ions containing more than five $3d$ electrons. In other words, the experimentally determined moments have a value which almost always lies evenly between the calculated value for μ_J (actual $\Delta\nu$) and μ_S. An obvious explanation of this is that the perturbing effect of the surrounding atoms is not large enough to completely destroy the angular moment. The residual orbital angular momentum is of great importance in explaining magnetic anisotropy, departures from Curie's law and the

TABLE V

Magnetic Moments of Iron Group Ions

Ion	Normal State	Theoretical Moment				Observed Moment (Solution), μ_B	Solid Salts	Observed Moment (Solid State), μ_B	Complex Solid Salts	Observed Moment (Solid State), μ_B
		$\Delta\nu=0$	$\Delta\nu=\infty$	$\Delta\nu$ Obs. Van Vleck	'Spin only', μ_S					
K^+, Ca^{++}, Sc^{+++}, Ti^{++++}	$3d^0\,{}^1S_0$	0·0	0.0	0·0	0·0	0·0	..	..	..	..
V^{++++}	$3d^2\,{}^2D_{3/2}$	3·0	1·55	1·78	1·73	1·75	..	..	..	..
V^{+++}	$3d^2\,{}^3F_2$	4·47	1·63	2·73	2·83	2·76-2·85	..	..	..	..
V^{++}	$3d^3\,{}^4F_{3/2}$	5·20	0·77	3·60	3·88	3·8-3·9	$Cr_2O_3 . 7H_2O$	3·85	..	..
Cr^{+++}	,,	,,	,,	2·97	,,	,,	$CrCl_3$	3·81	..	..
Cr^{++}	$3d^4\,{}^5D_0$	5·48	0·0	4·25	4·90	4·8-4·9	..	..	..	..
Mn^{+++}				3·80						
				5·92			$MnCl_2$	5·75	..	..
Mn^{++}	$3d^5\,{}^6S_{5/2}$	5·92	5·92		5·92	5·8	$MnSO_4$	5·87	..	..
Fe^{+++}				5·92			$MnSO_4 . 4H_2O$	5·87	..	..
							$Fe_2(SO_4)_3$	5·86	..	..
							$(NH_4)_2Fe_2(SO_4)_4$	5·86	..	..
				6·54			$FeCl_2$	5·23	$Fe(N_2H_4)_2Cl_2$	4·87
Fe^{++}	$3d^6\,{}^5D_4$	5·48	6·70		4·90	5·3	$FeCl_2 . 4H_2O$	5·25	..	..
				..			$FeSO_4$	5·26	..	..
							$FeSO_4 . 7H_2O$	5·25	..	..
							$(NH_4)_2Fe(SO_4)_2 . 6H_2O$	5·25	..	..
Co^{++}	$3d^7\,{}^4F_{9/2}$	5·20	6·64	6·56	3·87	5·0-5·2	$CoCl_2$	5·04	$Co(N_2H_4)_2SO_3 . H_2O$	4·31
							$CoSO_4$	5·04-5·25	$Co(N_2H_4)_2(CH_3COO)_2$	4·56
							$CoSO_4 . 7H_2O$	5·06	$Co(N_2H_4)_2Cl_2$	4·93
							$(NH_4)_2Co(SO_4)_2 . 6H_2O$	5·00	..	..
Ni^{++}	$3d^8\,{}^3F_4$	4·47	5·59	5·56	2·83	3·2	$NiCl_2$	3·24-3·42	$Ni(N_2H_4)_2SO_3$	3·20
							$NiSO_4$	3·42	$Ni(N_2H_4)_2(NO_2)_2$	2·80
									$Ni(NH_3)_4SO_4$	2·63
									$Ni(C_2H_4(NH_2)_2)_2(SCN)_2 . H_2O$	2·63
Cu^{++}	$3d^9\,{}^2D_{5/2}$	3·0	3·55	3·53	1·73	1·9-2·0	$CuCl_2$	2·02	$Cu(NH_3)_4(NO_3)_2$	1·82
							$CuSO_4$	2·01	$Cu(NH_3)_4SO_4 . H_2O$	1·81
Cu^+ Zn^{++}	$3d^{10}\,{}^1S_0$	0·0	0·0	0·0	0·0	0·0	..	..	..	..

Note.—The values for $\Delta\nu=0$, $\Delta\nu=\infty$ and 'actual' $\Delta\nu$ are the corrected values given by Van Vleck. The values under $\Delta\nu$ obs. have been calculated according to equation 42 of Chapter VII.

deviation of the susceptibility from the Bose-Stoner 'spin only' value (cf. Chapter VII, Sec. 13*b*)

$$\chi_M = \frac{4N\beta^2 S(S+1)}{3kT} \qquad . \quad . \quad . \quad (1)$$

Further, since the interaction is not so strong as to destroy the *L* moment completely, the atoms Fe^{++}, Co^{+++}, Co^{++}, Ni^{++}, Cu^{++} in aqueous solutions as well as in some crystalline salts do not form strong electron-pair bonds with H_2O, Cl, etc.

A case of particular interest is that of Fe^{+++} and Mn^{++} ions. These ions differ from others of the iron group in that they are in ^6S state and should have no angular momentum if there is ideal Russell-Saunders coupling. As a consequence these ions should be more isotropic and should conform more closely to the Bose-Stoner 'spin value' (Eq. 1) than the other members of this group. To a certain extent this is borne out by experiment and Mn^{++} gives a fairly constant magneton number 5·87. Van Vleck and Penny[36] in a recent paper have fully considered the deviations from the 'spin only' value as shown by the existence of anisotropy (cf. Chapter XII, Sec. 7) and by departures from Curie's law at low temperatures. The possibility of Heisenberg exchange effect being one of the causes for difference of the observed susceptibility of solid manganous compounds from the theoretical value is excluded, since the interatomic magnetic interaction of this kind is too small to account for most of the experimental departures from equation (1). The explanation of the deviation from (1) in magnetically 'dilute' manganous salts, according to Van Vleck and Penny, lies in the higher order approximations in the crystalline potentials as used by Kramers[37], Bethe[38], Van Vleck[39] and Penny, and Schlapp[40]. It is calculated that in the particular case of *S* states the mean susceptibility should obey Curie's law with great precision, but the individual principal susceptibilities along the *x*, *y* and *z* axes may show departures from Curie's law. Sometimes even when Curie's law is valid as in manganous and ferric salts the measurements are found to yield an effective Bohr magneton number different from the theoretical value $\mu_S = \sqrt{4S(S+1)} = 5{\cdot}92$ (for ^6S states). There could be two possible theoretical causes: (1) that even in the free gaseous state the ions Fe^{+++} and Mn^{++} may not have ideal Russell-Saunders coupling owing to distortion by spin-orbit forces, and (2) that the crystalline potential intermingles states of different orbital angular momentum which may cause distortion. Van Vleck and Penny are, however, of opinion that crystalline imperfections and experimental error are primarily responsible for the observed discrepancies. In the case of the other ions which are not in S states the deviations of the Curie constants from the Bose-Stoner values are quite appreciable and vary not only with the salt used but also with the crystalline axes.

In discussing the temperature variation of susceptibility in Chapter VII, Sec. 2, mention was made of the fact that the Curie law

$$\chi = \frac{C}{T} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

had a rather limited applicability and the Weiss formula

$$\chi = \frac{C}{T - \Delta} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

represented the observed temperature-susceptibility variations for a large number of substances. In most salts of the iron group in particular, the Weiss law holds well down to a certain critical temperature. Weiss sought to interpret Δ on the concept of intrinsic molecular fields, but it is possible now to discuss it more critically. If a number of compounds in which a paramagnetic atom has the same valency are examined, it is found that unlike the magneton number μ_{eff}, which remains comparatively constant, Δ is subject to marked variations, e.g. many of the chlorides of the iron group give a positive and sulphates a negative Δ value. Further, Δ is usually a slowly varying function of temperature, and in the case of solutions shows complicated variations with acid content, dilution and temperature interval, etc. It appears quite clear, therefore, that Δ is not an atomic property but arises primarily from distortions by interatomic forces, e.g. the Heisenberg exchange effect and the interaction of the orbital angular momentum. It could be shown as a deduction from Heisenberg's theory (cf. Van Vleck—*Electric and Magnetic Susceptibilities*, chapter xii) that the exchange forces between paramagnetic ions could effect the Δ variation to give a formula of the Weiss type (Eq. 3), but so far as the ordinary salts are concerned the contribution of exchange forces is very small and should, at any rate, vanish when the magnetic dilution is high as in hydrated sulphates, ammono-sulphates, etc. If exchange effect were the only factor operating these salts should have $\Delta = 0$, but this is far from being the case. While part of Δ arises from exchange effect, the balance has, undoubtedly, to be attributed to the distortion effects involving the orbital momentum. As an experimental check we turn to Mn^{++} and Fe^{+++} ions discussed above. These ions being in S state are devoid of orbital angular momentum, and consequently in salts involving these ions Δ should depend entirely on the Heisenberg exchange effect. Further, this effect would also disappear if the 'magnetic dilution' is large. This is verified beautifully for $MnSO_4.(NH_4)_2SO_4.6H_2O$ and $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ in which Δ is zero within the experimental error, and the simple Curie law holds down to the temperature of liquid hydrogen without any irregularity. Such exquisitely simple relations do not, however, obtain in the case of solutions of these salts. Even at large dilutions Δ does not seem to vanish completely. This could be capable of theoretical explanation if we assume that the compounds tend to form associated clusters or groups which maintain their identity at all dilutions. This view is confirmed by other physicochemical data in certain instances. It is, however, far from clear whether the clusters are simple associated molecules or possess a more complex structure. The large dependence of Δ on the nature of the negative radical seems to emphasise a complex formation. Mn^{++} ion which conformed to simple Curie law with compounds in the solid state was found by Cabrera and Duperier[41] to have Δ about 23 to 28 in aqueous solutions, though one would suppose that being in ^6S state when free, it may not be much affected by the surrounding water molecules.

The argument for the partial or total vanishing of the orbital moment made Pauling put forward the interesting view that the formation of the electron-pair bond will certainly destroy the orbital moment, and hence the magnetic moments of the molecules will also be given by the simple equation for members of the iron group.

The expression $\mu_B = \sqrt{4S(S+1)+L(L+1)}$, corresponding to Van Vleck's $\Delta\nu \ll kT$, has been successfully employed by S. Sugden[42] in explaining the susceptibilities of uni- and bivalent copper and silver compounds. In the univalent condition, the ions of these elements possess a complete sub-group of ten electrons (in the $3d$ level for copper and $4d$ level for silver), hence they should be diamagnetic. The bivalent ions will have only nine electrons in this sub-group and should therefore be paramagnetic. For such a sub-group Pauli's exclusion principle gives $S=1/2$ and $L=0$, 1 or 2, hence μ_S must be equal to 1·73 and $\mu_B=1\cdot73$, 2·24 or 3·00. The univalent compounds have been shown to be diamagnetic, whilst Sugden has shown that the bivalent atoms of these elements exhibit moments of 1·72-2·16 Bohr magnetons in fair agreement with the theoretically predicted value.

An interesting extension of theoretical principles has been made by Kenyon and Sugden[43], who have prepared a purely organic compound $C_{18}H_{22}O_2N_2$ from $COMe_2$ and NHPh.OH, which is diamagnetic, whilst its oxidation product $C_{18}H_{21}O_2N_2$, believed to contain N^{IV} or O^{I}, is strongly paramagnetic. The molecule has a moment close to 1·73 Bohr magneton corresponding with one unbalanced electron. Also, Asmussen[44] has recently described that the yellow salt of the formula $[(KSO_3)_2NO]_2$ which is obtained by the alkaline oxidation of hydroxylamine disulphonic acid has a feeble paramagnetism in the solid state while its blue aqueous solution gives approximately the theoretical paramagnetism for an odd molecule. This is ascribed to the change:

$$\text{(solid) } (KSO_3)_4N_2O_2 \rightleftharpoons 2(KSO_3)_2NO \text{ (solution)}$$

Sugden[45] has ingeniously employed susceptibility measurements for deducing evidence in favour of the existence of free radicals in organic compounds. The free radicals have been defined as substances whose molecules contain an odd number of electrons, although some free radicals with an even number such as CH_2 have also been reported. After correcting for diamagnetism of other constituents Sugden and his collaborators have established paramagnetism in the case of the following free radicals:

α-Naphthyl diphenyl methyl; $C_{18}H_{21}O_2N_2$; phenyl p-diphenylyl ketone potassium, and benzophenone potassium.

III. *Complex Molecules*

13. CO-ORDINATION COMPLEXES

There are on record a number of unsuccessful attempts to explain the structure of the co-ordination compounds (cf. Kossel and Briggs[46]). The first successful step towards elucidation of these complexes on electronic structure was taken by Sidgwick[47]. According to him, during the process of the formation of a co-ordination compound the central atom tends to assume the external electronic configuration of the next higher inert gas and the co-ordinated atoms, groups or molecules are attached by covalency to the central nuclear atom. This interpretation of Sidgwick has been accepted, notably by Lowry[48], Fowler[49], Spiers[50], Welo and Baudisch[51], Bose[52], Ray[53], etc. Butler[54], however, is not in complete agreement with Sidgwick, and assumes that the electrons contributed by the co-ordinated units form a distinct group round the central ion, meaning thereby that the co-ordination electrons enter the main quantum group next to that represented in the central ion. Such an assumption is a possibility, although there is no physical conception behind this speculation.

14. WELO AND BAUDISCH RULE

We shall refer now to the lead given by Welo and Baudisch in elucidating the magnetic properties of these compounds on the above concepts of Sidgwick. They have brought into prominence the fact that the complex compounds whose effective atomic number is equal to that of the next higher inert gas exhibit diamagnetism as they form closed configurations like those of the latter. They also showed that complex compounds whose effective atomic number falls short of or exceeds the inert gas configuration exhibit paramagnetism. In this manner, following Sidgwick, they have calculated the total number of electrons by adding to the atomic number the net number of shared electrons and get the following values: $Cr^{+++}=33$, $Fe^{+++}=35$, $Fe^{++}=36$, $Co^{+++}=36$, Ni^{++} (six-fold)$=38$, Ni^{-} (four-fold)$=34$ and $Cu^{++}=35$. The number thirty-six corresponds to the atomic number of argon, the next higher rare gas. The structure of the central atom is thus assumed to be that of argon, and on this concept it should be diamagnetic, which actually is the case; those in which the number falls short of or exceeds are paramagnetic, which again accords with experimental facts.

L. C. Jackson[55] has criticised this scheme as being arbitrary with no physical significance. For example, he shows that Welo and Baudisch by assigning five of the available electrons to N level of the chromium atom in the complex salts and four to the M level have made this atom simulate the structure of the divalent cobalt ion in its simple salts. Experimentally the Weiss magneton number for divalent cobalt is between twenty-four and twenty-five and for Cr^{+++} in complex chromium compounds nineteen. This disagreement is explained by stating that cobalt is anomalous, having a value of 19·2, when it is in the *S* state as quoted by Sommerfeld. This explanation is artificial as it is difficult to consider that divalent cobalt can be in the *S* state.

15. BOSE'S RULE

D. M. Bose[56] has gone a step forward and assumes that the magnetic moments of complex salts expressed in terms of Bohr magnetons are mostly proportional to the difference between their effective atomic number and the atomic number of the next higher inert gas. This and the Welo-Baudisch rules both afford considerable support to the Sidgwick concepts of the structure of a co-ordination compound.

According to Bose, the effective atomic number Z' of the co-ordinating atom in any complex compound is the sum total of all the electrons contained in the former plus the number of electronic orbits which this atom shares with the neighbouring atoms and groups in the co-ordination compound. Bose has further shown that $Z' = N - E + 2P$, where N = atomic number of the co-ordinating atom, E = its primary valency in the given compound and $P = 4, 6$, etc., according as the compound is four-fold, six-fold, etc. For example, in the ferrous compound $K_4[Fe(CN)_6], 3H_2O$, $Z' = 26 - 2 + 2 \times 6 = 36$, while in the case of the four-fold compound of copper $(Cu(NH_3)_4)(NO_3)_2$ $Z' = 29 - 2 + 2 \times 4 = 35$. Precisely similar numbers are obtained by calculating the effective atomic number from Sidgwick's rule.

Again, Bose has shown that $Z - Z' = n$, where Z is the atomic number of the next rare gas and Z' the effective atomic number of the co-ordinating atom and n the number of Bohr magnetons. Bose shows that this rule holds for a large number of compounds as in Table VI.

There are, however, several exceptions, particularly in complexes which are less perfect. Reference must be made here to the scheme of electron distribution amongst the various sub-groups of the main quantum groups for elements of the first transitional series and their ions, which has been proposed by D. M. Bose and which, according to him, satisfactorily explains their magnetic

TABLE VI

ILLUSTRATING BOSE'S RULE

Compound	Experimental Magneton Number		Effective Atomic Number		
	Weiss p	Bohr *	Z′	Z	Z − Z′
$(Cr(NH_3)_6)I_3$ . .	19	3 (19·2)	33	36	3
$(Fe(CN)_6)K_4\ 3H_2O$	0	0	36	36	0
$(Fe(CN)_6)K_3$ . .	10	1 (8·6)	35	36	1
$(CO(NH_3)_6)Cl_3$.	0	0	36	36	0
$(Ni(NH_3)_4)SO_4$.	13	2 (14·1)	34	36	2
$(Ni(NH_3)_6)SO_4$.	16	2·5 (16·7)	38	36	2
$(Cu(NH_3)_4)(NO_3)_2$.	9	1 (8·6)	35	36	1

* We have left unchanged in this and the following, the authors' original tables and results which were based on the older system of spectral classification (cf. Chapter V, Sec. 3).

According to the old Sommerfeld formula $p = 4{\cdot}978\sqrt{b(b+2)}$ where b is the number of Bohr magnetons for a single valence electron in $k=1$ orbit (cf. Stoner's *Magnetism and Atomic Structure*, p. 162).

moments. This scheme is of particular interest as it is possible to build upon it a design for electron distribution in the case of complex compounds of Fe, Co, Ni, Cr and Cu. The following table summarises the results given by Bose for electron distribution in the case of complex compounds:

TABLE VII

ELECTRON DISTRIBUTION SCHEME FOR TRANSITION ELEMENTS ACCORDING TO BOSE

Atom or Ion	Kind of Compound	Distribution of Electrons							Effective Atomic Number		Diff.	Co-ord. Number
		M		N			O		Ion	Co-ord. Atom		
		32	33	11	21	22	11	21				
Cr	Simple		3						21		12	6
	Complex	4	3	2	2	4				33		
Fe	Simple		4	1					23		12	6
	Complex	4	6	1	2	4				35		
Fe	Simple		4	2					24		12	6
	Complex	4	6	2	2	4				36		
Fe	Carbonyl	4	6	2	2	4				36		
Co	Simple	2	4						24		12	6
	Complex	4	6	2	2	4				36		
Ni	Simple	2	6						26			
	Complex	2	6	2	2	4				34	8	4
	Complex	2	6	2	2	4	2	2		38	12	6
Ni	Carbonyl	4	6	2	2	4				36		
Cu	Simple	2	6	1					27		8	4
	Complex	4	6	1	2	4				35		

From the scheme of distribution of electrons among the M_{32} and M_{33} sub-groups in the elements and ions of the transition group, Bose has extended his rule in the following manner.

$M_{33}+N_{11}-M_{32}=n$, in which M_{33}, N_{11}, etc., represent the number of electrons in the sub-group and n=number of Bohr magnetons. This modified rule of Bose has some physical significance and merits attention.

Bose's scheme is not supported by purely chemical evidence as he introduces a differentiation in the co-ordinated units by placing the shared electron pairs among different sub-groups of M—N quantum groups. Werner has shown that in the case of perfect complexes the equivalence of the co-ordinates is a fact beyond question and such cannot be the case if there is a difference of the co-ordination units as postulated by Bose. The scheme has been criticised by Ray[57] and Jackson[58], although their arguments are not formidable.

16. CABRERA'S RULE

Another scheme for the distribution of electrons in co-ordination compounds has been proposed by Cabrera[59]. He has made use of the scheme put forward by Fowler[49], who proposed that electrons outside the K and L levels of a six-fold co-ordinating atom have a tendency to be distributed in the groups 8+6+12. The first eight electrons are those occupying the M_{11}, M_{21} and M_{22} sub-groups of the atom, the next six tend to collect into the M_{33} sub-group and remaining twelve electrons are shared by the central atom and the groups surrounding it.

These electrons are made up of those contributed by various groups according to Sidgwick's rules together with the valency electrons of the central atom. Thus in Fe^{++} this group will consist of 10+2, in Cr^{+++} of 9+3 electrons. According to this scheme there is no need to postulate the tendency of the central atom to simulate the structure of the next higher inert gas, and the group of twelve electrons divided into two sub-groups of six each representing the six co-ordination units in the case of six-fold co-ordination compounds, or a group of eight electrons divided into two such groups of four each for the four-fold co-ordination, are arranged in a separate group after the M quantum group. This group of twelve electrons is assumed to possess as a whole no magnetic moment. The distribution of electrons in the ions of the six-fold and four-fold co-ordination compounds in this scheme is shown in the following table.

TABLE VIII

ELECTRON DISTRIBUTION OF TRANSITION ELEMENTS ACCORDING TO CABRERA

Ion	Number of Electrons					Binding Electrons
	M_{11}	M_{21}	M_{22}	M_{32}	M_{33}	
Cr^{+++}	2	2	4	..	3	12
Co^{+++}, Fe^{++}	2	2	4	..	6	12
Ni^{++}	2	2	4	2	6	12
Fe^{+++}	2	2	4	..	5	12
Ni^{++}	2	2	4	4	4	8
Cu^{++}	2	2	4	4	5	8

We see from this table the tendency of the M_{33} sub-group to fill to completion at the expense of M_{32}. In the case of Cr^{+++}, M_{32} sub-group has no electrons so that M_{33} remains incomplete and the ion has the same structure as the ion in simple salts. In Co^{+++} and Fe^{++} two electrons go from the M_{32} to the M_{33} sub-group, making it complete with six electrons. Thus the absence of electrons in M_{32} sub-group and the completion of the M_{33} level would make the co-ordination compounds of Co^{+++} and Fe^{++} diamagnetic, which agrees with the facts.

In the case of the complex ferro- and ferricyanides, we may suppose that the M_{33} sub-group tends to complete itself with six electrons. It can, however, only obtain five, as shown above for Fe^{+++}. These substances are therefore expected to be paramagnetic and to possess a magneton number equal to that of the simple cupric salts, since the structures of the ions are the same except for the M_{32} sub-group. Since the latter is unoccupied in the ferro- and ferricyanides and complete in the cupric ion, the net result is identical in both the cases and both groups of compounds possess nearly ten Weiss magnetons. The scheme for electron distribution for the four-fold co-ordination compounds of Ni^{++} and Cu^{++} is also shown in the above table. In these cases there are eight binding electrons or four pairs, which, following Werner and Sidgwick, are associated with points lying in a plane and occupying in the case of compounds in which the four groups are all similar, the corners of a square. Arguing from analogy with the six-fold compounds, it may be supposed that the M_{32} sub-group when complete possesses four electrons, and will, for this reason and also because of the four-fold arrangement of the outer binding electrons, tend to be completed at the expense of M_{33}. Cabrera, therefore, assumes that Ni^{++} has four electrons in both M_{32} and M_{33} in place of two in M_{32} and six in M_{33}, as in the case of simple nickel salts. Also Cu^{++} possesses four electrons in the M_{32} sub-group and the structure of this ion (four-fold complex) is the same as that of the simple cupric salts.

The above scheme of Cabrera has been supported in preference to the two other propositions by Jackson, who has modified the method of explanation for the four-fold compounds, and has also extended Cabrera's scheme to include multinuclear co-ordination compounds.

Cabrera's scheme, briefly speaking, implies that paramagnetism in complex ions develops when any sub-group in the main quantum groups of the central atom does not contain its full quota of electrons. Consequently a completed or wholly vacant sub-group develops diamagnetic property.

Cabrera's arrangement has, however, no physical significance behind it. The fundamental principle of the tendency of external electrons to 'ape' the next higher inert gas structure has been entirely ignored, and the scheme does not, therefore, follow the more or less generally accepted and uniform plan of atom-building. This scheme, although it assigns similar configurations to both Fe^{+++} and Mn^{++} ions, is unable to explain why manganous compounds are unstable whilst the corresponding ferric complexes are so very stable and well defined.

17. RAY'S INVESTIGATION ON COMPLEX COMPOUNDS

P. Ray has recently examined in a thorough manner the physical and chemical properties of the complex compounds. This investigation has led him to divide the complex compounds into two main classes which he calls strong or perfect and weak or imperfect complexes. The perfect or strong complexes include all six-fold complexes of cobaltic cobalt, a number of six-fold complexes of ferrous and ferric iron, all six-fold and four-fold complexes of platinum and the six-fold complexes of chromic chromium, tervalent rhodium, tri- and tetravalent irridium and a few ruthenium compounds. The above compounds manifest extraordinary complexity and characteristic chemical behaviour. The imperfect or weak complexes behave as if they were a transition between the double or associated compounds and the true complexes. It is for the first class of compounds that the scheme of electron distribution by Sidgwick is applicable. Ray, assuming with Ladenburg[60] that it is only the incompleted groups that contribute to the magnetic moment, has drawn up a scheme of electron distribution in the case of simple compounds. He further assumes that an odd electron in the M_{33} sub-group is very mobile specially at the commencement of the formation of the group and readily acts as a valency electron, whereas every two electrons tend to produce a more or less stable complexity, the stability of a group on the whole increasing with the number of electrons in it. Ray's scheme is shown in Table IX. It closely follows the principles laid down by Hund, who does not distinguish between the M_{32} and M_{33} sub-groups. But as such a subdivision becomes necessary from the chemical standpoint, Ray assumes with some justification that during chemical union largely dependent upon affinities and other external physical factors, the M_3 group may split up into M_{32} and M_{33} in a variety of ways. The atom may thus be regarded to pass into an active phase during chemical union.

TABLE IX

ELECTRON DISTRIBUTION SCHEME OF P. RAY

Atoms and Ions	Electron Number	Number of Electrons in Different Groups					Bohr's Magneton Number
		K_{11} to M_{22}	M_{32}		M_{33}	N_{11}	
Cr	24	18	..	4	..	2	..
Cr++	22	18	3	..	1	..	4
Cr+++	21	18	3	..	..	..	3
Mn	25	18	..	5	..	2	..
Mn++	23	18	1	..	4	..	5
Fe	26	18	..	6	..	2	..
Fe++	24	18	3	..	3	..	4
Fe+++	23	18	3	..	2	..	5
Co	27	18	..	7	..	2	..
Co++	25	18	3	..	4	..	4
Co+++	24	18	(*a*) 4	..	2	..	2·5
			(*b*) 3	..	3	..	..
Ni	28	18	..	8	..	2	..
Ni++	26	18	4	..	4	..	2
Cu	29	18	..	9	..	2	..
Cu+	28	18	4	..	6	..	0
Cu++	27	18	4	..	5	..	1

NOTE.—In the case of cobaltic ion it will be noticed that it behaves as a mixture of two electronic isomers, which thus account for its anomalous magnetic behaviour.

18. LINUS PAULING'S THEORY FOR COMPLEX MOLECULES

L. Pauling[61] has given particular attention to the peculiar behaviour of the complex ions. He finds that there are many exceptions to the Bose-Sidgwick rule. For example, $[Ni(CN)_4]^{--}$ is diamagnetic, while on the above rule it should have the same paramagnetic moment as $[Ni(NH_3)_4]^{++}$. Pauling has tried to clarify the subject on the quantum mechanical treatment of the nature of the chemical bond, which permits conclusions to be drawn regarding the type of bond in many molecules and complex ions from a knowledge of their magnetic moments, and conversely provides the basis for finding the magnetic moment from a knowledge of the type of bonds and the atomic arrangement.

On spectroscopic and quantum mechanical considerations Pauling deduces that the elements in the iron group should obey the following rules:

(i) For atoms of this group, bond eigenfunctions should be formed from the nine eigenfunctions $3d^5$, $4s$ and $4p^3$, and one bond eigenfunction should be needed for each electron-pair bond.

(ii) The remaining unshared electrons should be introduced into the $3d$ eigenfunctions not involved in bond formation.

(iii) The normal state should correspond to the state with the maximum resultant spin S allowed by the Pauli principle.

The above rules apply to the palladium group (eigenfunctions $4d^5 5s 5p^3$) and the platinum group (eigenfunctions $5d^5 6s 6p^3$).

On a consideration of the eigenfunctions it is shown that all cannot be equivalent, but six equivalent bonds extending towards the corners of either a regular octahedron, or a trigonal pyramid, four extending towards the corners of a tetrahedron or a square, etc., can be formed. According to Pauling, in the complexes in which the central atom forms a co-ordinated octahedron of six atoms or groups the bonds may be any of the several types, each of which requires a different treatment:

(i) All bonds ionic or ion-dipoles: The moments then should be given by the figures shown in column I (Table X).

(ii) Four electron-pair bonds may be formed, which should be of the type dsp^2 and lie in a plane. The moments are then given by column II.

(iii) Six electron-pair bonds may be formed, leaving only

TABLE X

PREDICTED MAGNETIC MOMENTS OF COMPLEXES CONTAINING TRANSITION ELEMENTS (PAULING)

Ions			I	II	III	IV
			For Ion or $4sp^3$ Bonds	For 4 dsp^2 Bonds	For 6 d^2sp^3 Bonds	For 8 d^4sp^3 Bonds
K^1 Ca^2 Sc^3 Ti^4, etc.	Rb^1 Sr^2 Y^3 Zr^4 Nb^5 Mo^6	Cs^1 Ba^2-Hf^4 Ta^5 W^6	0·00	0·00	0·00	0·00
V^4	Nb^4 Mo^5	W^5	1·73	1·73	1·73	1·73
V^3 Cr^4	Mo^4 Ru^6	W^4 Os^6	2·83	2·83	2·83	0·00
V^2 Cr^3 Mn^4	Mo^3		3·88	3·88	3·88	. .
Cr^2 Mn^3 Fe^4	Mo^2 Ru^4	Os^4	4·90	4·90	2·83	. .
Mn^2 Fe^3 Co^4	Ru^3	Os^3 Ir^4	5·91	3·88	1·73	. .
Fe^2 Co^3	Ru^2 Rh^3 Pd^4	Ir^3 Pt^4	4·90	2·83	0·00	. .
Co^2 Ni^3	Rh^2		3·88	1·73	. .	. .
Ni^2	Rh^1 Pd^2 Ag^3	Pt^2 Au^3	2·83	0·00	. .	. .
Cu^2			1·73	. .	. .	. .
Cu^1 Zn^2 Ca^3 Ge^4, etc.	Ag^1 Cd^2 In^3 Sn^4 Sb^5 Te^6	Au^1 Hg^2 Tl^3 Pb^4 Bi^5 Po^6	0·00	. .	. .	. .

three eigenfunctions for the additional electrons. In this case the moments are given by figures in the third column.

(iv) Eight electron-pair bonds may be formed involving the eigenfunctions d^4sp^3. The magnetic moments in this case are given by column IV of the table.

It will be seen from the table that the complex salts have magnetic moments which can be approximately represented by the equation

$$\mu_B{}^2=4S(S+1)$$

if S is given a suitable value. For example, the complex copper salt $[Cu(NH_3)_4(NO_3)_2]$ has a magneton number somewhere between 1·75 to 2·0, $Ni(NH_3)_6Br_2$ has a value of 2·6 to 3·2, and $Cr(NH_3)_6I_3$ a value of 3·4 to 3·8. If we assign to S the values 1/2, 1 and 3/2, we get the figures 1·73, 2·83, 3·87, which agree fairly satisfactorily with the observed values. These are just the values of the isolated Cu^{++}, Ni^{++} and Cr^{+++} ions, and this shows that even in complex salts the iron group ions are capable of fairly independent existence. A large number of complex molecules show that they are diamagnetic or very feebly paramagnetic. In these cases obviously the resultant spin S of the complex ion has a zero value.

In Table XI the magnetic moments of a number of complex molecules are given for reference. We may consider from it, for example, the magnetic moments of the Mn complexes $[Mn(CN)_6]^{---}$ and $[Mn(CN)_6]^{----}$ which have the values 3·01 and 2·0 respectively. On referring to the last table we find that the nearest values to 3·01 and 2·0 are 2·83 and 1·73 respectively, and that Mn^2 ion has the value 1·73 for six electron-pair bond, and also Mn^3 has the value 2·83 for the six electron-pair bond. We deduce, therefore, that both bivalent and trivalent manganese forms six electron-pair bonds with (CN) groups. Similarly, bivalent and trivalent chromium, iron and cobalt are also found to form six electron-pair bonds with (CN) group and also with other groups such as NH_3, Cl and NO_2.

The observed diamagnetism of the ions $[Mo(CN)_8]^{----}$ and $[W(CN)_8]^{----}$ seems to indicate that the central atom forms eight electron-pair bonds involving the eigenfunctions d^4sp^3 in the fourth column of Table X.

The diamagnetism of $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$ can be easily explained on the Pauling theory. The nine eigenfunctions which are the characteristics of *dsp* couplings are

TABLE XI

OBSERVED MAGNETIC MOMENTS OF COMPLEX MOLECULES

Substance	Bohr Magneton, μ_B	Substance	Bohr Magneton, μ_B
		K_2PtCl_4	0·0
$Na_2\left[Fe\begin{matrix}(NO)\\(CN)_5\end{matrix}\right]2H_2O$	0·0	$K_2Pt(C_2O_4)_2\ 2H_2O$	0·0
		$Pt(NH_3)_4SO_4$	0·0
$K_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	0·0	$Rb_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	0·0
$(NH_4)_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	0·0	$Cs_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	0·0
$Tl_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	0·0	$Na_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]H_2O$	0·0
		$K_3Fe(CN)_6$	2·0
$\left[Co\begin{matrix}S_2O_3\\(NH_3)_5\end{matrix}\right]Cl$	0·0	$K_4Mn(CN)_6$	2·0
		$K_4Fe(CN)_6\ 3H_2O$	0·0
$K_3Co(CN)_6$	0·0	$Na_3Fe(CN)_5NH_3$	0·0
$K_4Co(CN)_6$	0·0	$K_3Co(CN)_6$	0·0
		$K_3MoCl_6.2H_2O$	3·0
$K_6\left[Co_2\begin{matrix}SO_3\\(CN)_{10}\end{matrix}\right]$	0·0	$(NH_4)_2(FeF_5.H_2O)$	5·97
		$(NH_4)_3Mo(SCN)_6.4H_2O$	3·0
		$K_4[Mo(CN)_8]$	0·0
$\left[Co\begin{matrix}(NH_3)_5\\(NO)\end{matrix}\right]Cl_2$ (black)	2·0	$K_4Mo(CN)_8.2H_2O$	0·0
		$K_4[W(CN)_8]2H_2O$	0·0
		$Na_3[IrCl_2(NO_2)_4]$	0·0
		$[Ir(NH_3)_5NO_2]Cl_2$	0·0
$\left[Co\begin{matrix}(NH_3)_5\\(NO)\end{matrix}\right](NO_3)_2.1/2H_2O$ (red)	0·0	$[Ir(NH_3)_4(NO_2)_2]Cl$	0·0
		$[Ir(NH_3)_3(NO_2)_3]$	0·0
		$K_2(PtCl_6)$	0·0
		$[Pt(NH_3)_6]Cl_4$	0·0
$K\left[Fe\begin{matrix}(NO)_2\\S_2O_3\end{matrix}\right]H_2O$	0·0	$[Pt(NH_3)_5Cl]Cl_3$	0·0
		$[Pt(NH_3)_4Cl_2]Cl_2$	0·0
$Cu(C_2H_5ON_4)_2.3H_2O$		$[Pt(NH_3)_3Cl_3]Cl$	0·0
Copper dicyandiamidine	1·0	$[Pt(NH_3)_2Cl_4]$	0·0
$Cu(C_2NO_2H_4)_2.H_2O$		$[Co(NH_3)_6]Cl_3$	0·0
Copper aminoacetate	1·0	$[Co(NH_3)_5Cl]Cl_2$	0·0
		$[Co(NH_3)_4Cl_2]Cl$	0·0
Tetra-kisethylene thio-carbamido cuprous nitrate	0·0	$Na_2[Fe(CN)_5NO]2H_2O$	0·0
$K_3Mn(CN)_6$	3·01	$[Ru(NH_3)_4.NO.H_2O]Cl_3$	0·0
$K_4Cr(CN)_6$	3·3	$[Ru(NH_3)_4.NO.Cl]Br_2$	0·0
$[Co(NH_3)_3(NO_2)_2]$	0·0	$[Co(NH_3)_5NO]Cl_2$	2·81
$[Co(NH_3)_5H_2O]_2(C_2O_4)_3$	0·0	$Ni(CO)_4$	0·0
$K_2Ni(CN)_4$	0·0	$Fe(CO)_5$	0·0
$K_2Ni(CN_4).H_2O$	0·0	$Cr(CO)_6$	0·0

completely filled in these cases by n carbonyl bonds and $2(9-n)$ additional electrons attached to the atom where $n=4, 5, 6$. If it is assumed that an electron-pair bond is formed with each carbonyl group it is easy to see that the number of electrons involved are

(*a*) for $Ni(CO)_4$ $\quad 2\times 4 \quad + \quad 2(9-4)=18$
$\qquad$ (for $(CO)_4$)
(*b*) for $Fe(CO)_5$ $\quad 2\times 5 \quad + \quad 2(9-5)=18$
$\qquad$ (for $(CO)_5$)
(*c*) for $Cr(CO)_6$ $\quad 2\times 6 \quad + \quad 2(9-6)=18$
$\qquad$ (for $(CO)_6$)

This shows that the electrons involved have the inert gas structure and the compounds should be diamagnetic.

It is also possible to stretch this theory in order to explain the composition or the possibility of formation of a particular metal carbonyl. The only assumption to be made is that (CO) molecules continue to add on as long as bond eigenfunctions are available. Take, for example, the case of iron: it has eight electrons in its outermost shells and requires ten more to complete the number required to fill up its nine eigenfunctions. As the addition of a carbonyl group is equivalent to an electron-pair bond or two electrons, it is clear that iron can form a carbonyl compound of the composition $Fe(CO)_5$ which would be diamagnetic. Similarly, cobalt has nine electrons in its outermost shells and requires nine more electrons to completely fill nine eigenfunctions. Thus it can have four carbonyl groups and a single electron to occupy all the nine eigenfunctions, thus predicting the existence of a compound of the composition $Co(CO)_4$ which would have one unbalanced electron and show a magnetic moment of 1·73. Similarly, the existence of $Mn(CO)_5$ and $V(CO)_6$ is predicted successfully. On this theory these compounds should have a magnetic moment of 1·73, which also is borne out by experiments.

This discussion gives an indication of the usefulness of the magnetic data in providing information regarding the nature of the chemical bond. It has also been shown that the quantum mechanical rules for electron-pair bonds are essential to the treatment.

Further, Pauling has given an explanation of the difference in magnetic susceptibilities of perfect and imperfect complexes on the basis of wave-mechanical principles. He assumes that the electronic 'eigenfunctions' of the central paramagnetic ion under the influence of strong chemical disturbance and penetration due to approach of other atoms may, in certain cases, be redistributed, giving rise to new 'eigenfunctions' different from the original ones in their form and binding capacities. The result of this redistribution is often an alteration in the magnetic property of the central ion. P. Ray adheres to the view that the valence bond in all the complex compounds should be regarded as of the co-ordinated covalent type, both the electrons of the shared pair in each bond being contributed by the co-ordinated unit or atoms. The electrons in the incomplete shell of the central ion consequently take no part in the formation of the bond. Ray[62] believes that it is impossible to explain on Pauling's view the constitution and behaviour of the hexa-co-ordinated nickel and cobaltous and copper complexes. The penta-co-ordinated copper compounds also present similar difficulties. There will not be sufficient '*d*-eigenfunctions' left in these cases for the allocation of unshared electrons, nor will it be easy to account for the magnetic properties of these compounds. The work of Linus Pauling, however, presents a sounder physical basis of this behaviour and is not of an empirical nature, which the various rules described above have necessarily to be. The simplicity of the attempts of Sidgwick, Bose and Ray at explaining the magnetic behaviour of the complex molecules * and the vast number of cases which are satisfactorily explained by them are features which promise a long lease of life to some of these rules.

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CHAPTER X

MAGNETO-OPTICAL PROPERTIES IN CHEMICAL INVESTIGATIONS

IN the chapter on Magnetism and Valency reference has been made from time to time as to how the values of magnetic susceptibility of elements and compounds can be utilised to get information on atomic and molecular structures. No book on magnetochemistry can be said to be complete without reference to the magneto-optical effects which have been so useful in elucidating structural problems in chemistry. The paucity of references to the memorable work of W. H. Perkin[1] and his pupils on magneto-rotatory behaviour of organic substances in books on magnetism is surprising. Perkin's investigations on this property have done more to arouse the interest of the chemist in the subject of magnetism than any other work in this branch of the subject, and it is proposed in this chapter to trace the history of the development of the subject of magneto-optics from the point of view of its importance to the chemist.

The following constitute the most important phenomena in this field: (*a*) the Faraday Effect, (*b*) the Magnetic Double Refraction or the Cotton-Mouton Effect, (*c*) the Kerr Effect and (*d*) the Zeeman Effect.

In the sections that follow the first three effects are discussed in detail, leaving the Zeeman effect, which is outside the scope of this book.

I. *The Faraday Effect*

Faraday[2] in 1846, while looking for a possible relation between electric and magnetic phenomena and those of light, discovered that a transparent body by itself inactive acquires the property of rotating the plane of polarisation of a beam of light when it is placed in a magnetic field. Faraday further showed that the rotation was maximum when the lines of force traversed the medium in the same direction as the beam of light and disappeared when the field was perpendicular to the direction of observation.

Two years after this discovery Mathiessen[3], in a series of papers, showed its occurrence in the case of liquids, and later, in 1879, Becquerel[4] succeeded in demonstrating that gases and vapours also when suitably observed in long columns rotated the plane of polarisation. The Faraday effect was thus proved to be a very general phenomenon.

The amount of rotation was found, by Wiedemann[5] and others, to be proportional to the length of the medium traversed and to the strength of the field.

The experiments of Kundt[6] and Du Bois[7] were mainly confined to ferromagnetic substances. The effect in these was so powerful that they observed it even in the case of films of iron which were so thin as to be transparent to ordinary light.

1. POSITIVE AND NEGATIVE FARADAY ROTATION

The direction of the rotation is determined by that of the magnetic force, and in the case of most diamagnetic substances is the same as that in which a positive current must circulate round the beam of light in order to produce the magnetic field that actually exists. There are, however, notable exceptions to the rule, that the rotation is positive for diamagnetic and negative for ferromagnetic media; for instance, oxides of manganese and salts of nickel and cobalt though paramagnetic give a positive rotation, while the diamagnetic potassium chromate and titanium bichloride produce a negative rotation.

The possibility of a close connection between the magnetic rotatory power of a substance and its index of refraction for light occupied the attention of several early workers. De la Rive[8] put forward the suggestion that magneto-rotation should increase with the refractive index of the medium, and this seemed to be confirmed by the experiments of Bertin[9]. Verdet's extensive work[10], performed under better conditions, however, failed to support this. On the other hand, he conclusively proved that though substances with a higher refractive index have in general larger rotatory power, there is no definite relationship between the two.

2. THEORIES OF MAGNETIC ROTATION

No completely satisfactory theory is yet available, although the classical treatment of Fresnel that a plane polarised vibration traversing the medium is resolved into two circular components which travel with different velocities thereby giving a rotation to the plane of polarisation found much favour. As early as 1851, Wiedemann [11] and others tried the effect of different wavelengths of light and showed that the rotation increases with decreasing wavelength, varying inversely as the square of wavelength. The experimental work of Verdet[10], Righi[12], and Becquerel[13] did much to clarify the phenomena, and the latter, in 1878, showed that gases as well exhibited the effect. Becquerel, however, was the first to clearly point out the relationship between the magneto-rotatory power on the one hand and the wavelength and refractive index on the other. Following Larmor, the formula could be deduced by making use of Larmor's theorem of precession of angular velocity (Chapter VI, Eq. 3) and a rather simple atomic model. If θ denotes the rotation produced by field H in a length l of the substance, Becquerel's formula can be written in the form:

$$\theta = \mathrm{C}l\lambda\frac{dn}{d\lambda}\mathrm{H} \quad . \quad . \quad . \quad . \quad (1)$$

where n and λ are the refractive index and wavelength, respectively, and $\mathrm{C} = \frac{e}{2mc}$ is a constant, c being velocity of light, e the electronic charge and m the mass.

The rotation produced by a unit field in a unit length (1 mm.) is known as *Verdet's constant* and is usually denoted by V. In terms of Verdet's constant the specific magnetic rotatory power can be defined by $\frac{\mathrm{V}}{\rho}$ where ρ is the density of the substance.

Becquerel's formula, though based on very simple considerations, served to express experimental results for a large number of substances, provided that λ was sufficiently removed from the position of an absorption band. Drude made use of the earlier electronic theory and deduced expressions not far different from Becquerel's formula, but taking into account the absorption bands. Recently Mallemann [14] has given a molecular theory of magnetic rotation, following the classical ideas of Lorentz. For a liquid Mallemann's theory gives $\frac{\mathrm{V}}{\rho} \cdot \frac{n}{(n^2+2)^2} = \text{constant}$, n being the refractive index. This expression has found excellent confirmation in the very recent work of Gabiano [15] on the vapours. Gabiano finds that the specific rotatory power of a vapour divided by that of its liquid gives the expression $\frac{9n}{(n^2+2)^2}$ which follows from Mallemann's formula. The expression has been verified for a number of substances such as benzene, carbon disulphide, methyl iodide, pentane, hexane, etc.

It is not possible to discuss here in any detail the more recent quantum mechanical interpretations of the Faraday Effect. Rosenfeld [16] has treated the case of free monatomic atoms on lines somewhat similar to Van Vleck's theory of para- and diamagnetism. A beginning for diatomic molecules was made earlier by Kronig [17] but an adequate theory is still wanting. It is, however, a noteworthy fact that Becquerel's formula with an anomalous value for C has been found to give rotations for a large number of molecules. This is equivalent to adding another constant K in the formula and keeping $C = \frac{e}{2mc}$ unchanged, and resembles in this form the extension proposed by Bhatnagar and his collaborators (Chapter VI, 2. iv) to account for molecules in Langevin's equation for diamagnetism. Darwin and Watson [18] have compiled a number of experimental values of the constant C and find the anomaly to range between 0·50 and 0·70. For H_2 it is 0·99, which means that Becquerel's formula holds unmodified. The behaviour of oxygen is entirely anomalous.

3. PARA- AND DIAMAGNETIC TERMS IN FARADAY ROTATIONS

In his quantum mechanical treatment Rosenfeld finds an expression for the Faraday rotation in monatomic systems. This expression is found to consist of two parts—one part independent of temperature and the other varying inversely with temperature. On analogy from susceptibilities Ladenburg [19] calls the first the diamagnetic and the second the paramagnetic part of the Faraday rotation. In order to express the results in simplified form Rosenfeld has considered three limiting cases: *

(*i*) *Multiplet width small compared to* kT *and incident light well outside the multiplet.*

Here the diamagnetic part has been found to be identical with Becquerel's formula. The paramagnetic part contains the expression $\frac{L(L+1)}{3kT}$. If the atom is in S state the factor $L(L+1)$ will vanish and consequently the paramagnetic part will completely disappear, even if spin paramagnetism is present ('spin only' value).

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* For further details see the original papers or Van Vleck's *Electric and Magnetic Susceptibilities*, chapter xiii, which contains an excellent summary.

(*ii*) *Incident light has wavelength very near to one particular multiplet.*

In this case the diamagnetic part is identical with Becquerel's formula but with an anomalous value for C, i.e. $C' = \frac{e}{2mc}K$. The paramagnetic part contains the factor $g_j{}^2\frac{J(J+1)}{3kT}$ and will in consequence be present even if the atom is in S state provided it has a spin moment. An interpretation of K based on the mean Zeeman displacement has been given by Kuhn[20].

(*iii*) *Multiplet widths large compared to kT and incident light outside the multiplet.*

Here Becquerel's formula is not obeyed even with anomalous value of C.

4. EXPERIMENTAL METHODS OF MAGNETO-OPTICAL ROTATION

The absolute magnetic rotation of a substance is defined as the rotation which the plane of polarisation undergoes when a beam of homogeneous plane-polarised light traverses a layer of unit length of that substance placed in a magnetic field of unit intensity. For the problems of structural chemistry it is not necessary to know the absolute value. All that is required is to know the value of the rotation expressed in terms of some standard substance under the same experimental conditions, and Perkin in his classical work on magnetic rotation has employed water as the standard.

The relative specific rotation is the ratio of the rotations produced by the substance under examination to the standard substance in layers of equal thickness at the same temperature and under the influence of the same magnetic field, and is given by the following expression:

$$r = \frac{a}{\alpha}$$

where r=relative specific rotation,
a=rotation of the substance,
α=rotation of water under the same conditions.

When the layers of the substance and the standard are not of the same length, r is given by the generalised expression

$$r=\frac{al'}{\alpha l}$$

where l is the length of the substance and l' of the standard.

In order to compare the rotations of different substances with one another we require to know the rotatory effects of equal number of molecules of the substances under examination. This is done by deducing the value of the molecular magnetic rotation M, which is equal to

$$M=\frac{al'}{\alpha l}\cdot\frac{m\delta}{\mu d}$$

where m = molecular weight of the substance,
d = density of the substance,
μ = molecular weight of the standard,
δ = the density of the standard.

Since in practice the same tubes are employed,

$$M=\frac{am\delta}{\alpha\mu d}$$

The presence of the factor $\frac{m}{d}$ shows that these relations hold only in the case of substances having the same molecular complexity and do not apply to substances which are associated.

5. Molecular Magnetic Rotation from Solutions

Sometimes it is convenient to work on the magnetic rotations of solutions. The rotation due to the dissolved substance can be calculated by noting the rotation of the solution and then by subtracting from it the rotation of the solvent. The formula for solutions is

$$M_S=\frac{(m+nm')al'\delta}{\alpha\mu l d}$$

where m and m' are the molecular weights of the substance and solvent respectively and n the molecular proportion of the solvent, so that $M=M_S-M'n$ where M, M_S and M' are the molecular rotations of the solute, solution and solvent and n is the proportionality factor.

When necessary the absolute rotation (R) of a substance can be derived by substituting the absolute rotation of the standard; if the latter be denoted by r, i.e.,

$$R=\frac{Mrd\mu}{\delta m}$$

The absolute rotation for water as given by Rodger and Watson[21] is

$$r=0{\cdot}01311-0{\cdot}0_{6}4t-0{\cdot}0_{7}4t^{2}$$

where t may vary between 4° and 98°.

Two forms of arrangement are generally employed in investigations on magnetic rotation. One consists in placing the body directly between the pole-pieces of an electromagnet. This arrangement with some modifications was extensively employed by Perkin in his classical experiments and is shown in Fig. 45. The other arrangement consists in winding a solenoid over an ordinary polarimeter tube. This method was employed largely in the later work of Rodger and Watson[21], of Siertsema[22] and of Bhatnagar, K. N. Mathur and Jain[23].

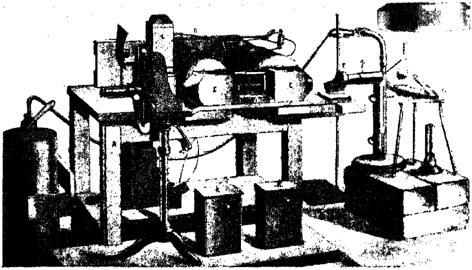


FIG. 45.—Perkin's arrangement for investigating magnetic rotation.

6. INFLUENCE OF TEMPERATURE

The temperature coefficient of molecular magnetic rotation is not large; and it is found that as a rule the rotation decreases with rise in temperature. In homologous series Perkin found that substances of higher molecular weight have greater effect than the simpler constituents of the series. The effect is more marked in aromatic than in aliphatic substances; for example, for acetic acid for a rise of 100° the change in molecular magnetic rotation is $-0{\cdot}049$, while for benzene it is $-0{\cdot}477$; for methylene iodide (CH_2I_2) it is $-0{\cdot}863$, while for α-naphthylamine it is $-1{\cdot}561$.

7. THE MAGNETO-ROTATORY EQUIVALENT FOR THE CH_2 GROUP IN HOMOLOGOUS SERIES

In order to study the additive relations Perkin studied the various homologous series, and Table I is adapted from his extensive researches and their excellent summary in Smiles'[24] *The Relations between Chemical Constitution and some Physical Properties* and Cohen's *Organic Chemistry*, Part II.

A glance at the table reveals the fact that the value for Δ, the increase in rotation due to the addition of CH_2, is almost constant in the different types of compounds considered. From the fact that the values of Δ vary slightly it is evident that constitutional effects also influence this value, though on the whole it is reasonably safe to strike an average which, according to Perkin, comes out to

$$\Delta_{\text{Mean}} = 1{\cdot}023$$

It will be noticed that as a rule the first member of the homologous series shows a larger divergence from the mean value of Δ than the next member of the series. This peculiarity of behaviour of the first member is common to other physical properties also. With the known value for the CH_2 group it is possible to calculate the rotation of any member of the series if the rotation of one of them is known accurately. Conversely it is possible to locate the right place of a member in the series from a knowledge of its magnetic rotation.

8. SERIES CONSTANT IN MAGNETO-OPTICAL ROTATION

Suppose in a particular group of compounds, a molecule belonging to that group has n carbon atoms, then by subtracting the value for nCH_2, i.e. $n \times 1{\cdot}023$, from the total magnetic rotation, a number called the 'Series Constant' is obtained which is nearly constant for the whole series of compounds in that particular group. The series constant is denoted by the letter 'S'.

TABLE I

Δ_{CH_2} FOR HYDROCARBONS

Substance	M_t	
Pentane	5·638	
Hexane	6·670	1·032
Heptane	7·669	0·999
Octane	8·772	1·103
Decane	10·998	2 × 1·113
Isopentane	5·750	
Isohexane	6·769	1·019
Alcohols—		
Methyl alcohol	1·640	
Ethyl alcohol	2·780	1·140
Propyl alcohol	3·678	0·898
Heptyl alcohol	7·850	4 × 1·043
Octyl alcohol	8·880	1·030
Aldehydes—		
Acetaldehyde	2·385	
Propaldehyde	3·332	0·947
Heptaldehyde	7·422	4 × 1·022
Ketones—		
Acetone	3·514	
Methyl propyl ketone	5·499	2 × 0·992
Dipropyl ketone	7·471	2 × 0·986
Acids—		
Formic acid	1·671	
Acetic acid	2·525	0·854
Propionic acid	3·462	0·937
Butyric acid	4·472	1·010
Valeric acid	5·513	1·041
Oenanthylic acid	7·552	2 × 1·019
Caprylic acid	8·565	1·013
Pelargonic acid	9·590	1·025
Acetic Esters—		
Methyl acetate	3·362	
Ethyl acetate	4·462	1·100
Propyl acetate	5·487	1·025
Octyl acetate	10·601	5 × 1·023
Cetyl acetate	18·772	8 × 1·021
Halogen Derivatives—		
Methyl iodide	9·009	
Ethyl iodide	10·075	1·066
Propyl iodide	11·080	1·005
Octyl iodide	16·197	5 × 1·023
Methyl bromide	4·644	
Ethyl bromide	5·851	1·207
Propyl bromide	6·885	1·034
Octyl bromide	12·025	5 × 1·028
Ethyl chloride	4·039	
Propyl chloride	5·056	1·017
Octyl chloride	10·128	5 × 1·014

As an illustration take the case of fatty acids:

	M	$n \times 1{\cdot}023$	S
Propionic acid	3·462	$3 \times 1{\cdot}023$	0·393
Butyric acid	4·472	$4 \times 1{\cdot}023$	0·380
Valeric acid	5·513	$5 \times 1{\cdot}023$	0·398
Oenanthylic acid	7·552	$7 \times 1{\cdot}023$	0·391
Caprylic acid	8·565	$8 \times 1{\cdot}023$	0·381
Pelargonic acid	9·590	$9 \times 1{\cdot}023$	0·383
			Mean=0·393

The first two members are omitted because they are abnormal.

The molecular magnetic rotation can now be calculated from the equation:

$$M = S + n(1{\cdot}023)$$

The series constants for different types of compounds as obtained by Perkin are shown below:

TABLE II

SERIES CONSTANTS (PERKIN)

Series	General Formula	S
Paraffins, normal	C_nH_{2n+2}	0·508
Paraffins, iso	C_nH_{2n+2}	0·631
Alcohols, primary	$C_nH_{2n+2}O$	0·699
Alcohols, iso	$C_nH_{2n+2}O$	0·844
Aldehydes	$C_nH_{2n}O$	0·261
Ketones	$C_nH_{2n}O$	0·375
Fatty acids	$C_nH_{2n}O_2$	0·393
Unsaturated acids	$C_nH_{2n-2}O_2$	1·451
Dibasic acids	$C_nH_{2n-2}O_4$	0·196
Formic esters	$C_nH_{2n}O_2$	0·495
Acetic esters	$C_nH_{2n}O_2$	0·370
Esters of higher acids	$C_nH_{2n}O_2$	0·337
Methyl esters	$C_nH_{2n}O_2$	0·273
Ethyl esters	$C_nH_{2n}O_2$	0·337
Alkyl chlorides	$C_nH_{2n+1}Cl$	1·988
Alkyl chlorides, iso and secondary	$C_nH_{2n+1}Cl$	2·068
Alkyl bromides	$C_nH_{2n+1}Br$	3·816
Alkyl bromides, iso and secondary	$C_nH_{2n+1}Br$	3·924
Alkyl iodides	$C_nH_{2n+1}I$	8·011
Alkyl iodides, iso and secondary	$C_nH_{2n+1}I$	8·099

9. Some Applications of Δ and Series Constants

The results in Table II can be utilised in the following manner:

Take for example the case of ethyl acetonedicarboxylate (Perkin):

The interest attaching to the examination of this substance consists in its representing ethyl acetoacetate with hydrogen of the methyl group replaced by a second carbethoxyl group, and as this is of a negative character, it is possible that it might influence the ketonic nature of the compound. It may exist as

$COOC_2H_5.CH_2.CO.CH_2.COOC_2H_5$ Ketonic, saturated,

or $COOC_2H_5.CH:C(OH).CH_2.COOC_2H_5$ Hydroxylic, unsaturated.

v. Pechmann,[25] who discovered this interesting substance, has discussed the question of its constitution from a chemical point of view and concluded that it must possess a ketonic formula. Bruhl,[26] who determined its refractive power, found it to behave as a saturated compound. Nef,[27] on the other hand, disputed the validity of v. Pechmann's conclusions. When examined magnetically the rotation of the compound confirmed to a great extent the views of v. Pechmann, showing that the substance was chiefly ketonic, but it also indicated that at ordinary temperatures it probably contains a small amount of an enolic or unsaturated isomer.

The rotation for the formula $COOC_2H_5.CH_2.CO.CH_2.COOC_2H_5$ may be calculated in any of the following ways:

(*a*) Molecular rotation for ethyl acetoacetate . .	6·501
Molecular rotation for $COOC_2H_5$ rep. hydrogen	2·951
	9·452
(*b*) or taking acetone as the basis of the calculation:	
Molecular rotation for acetone	3·514
Molecular rotation for $2COOC_2H_5$ rep. hydrogen	5·902
	9·416
(*c*) From the series constants it is:	
Series constant for the ester of dibasic acid (glutaric)	0·140
Series constant for ketone	0·375
Mean of the above	0·257
With $n=9$, . 1·023×9 . .	9·207
	9·464

The first and the last calculations come very close, giving an average value 9·444 from (*a*), (*b*) and (*c*).

The rotation determined at 16·5° gives 9·604 or 0·160 in excess of the calculated value; this is greater than the expected experimental error. The rotation was again determined at a higher temperature, and at 94° it gave 9·374 or 0·070 less than the calculated value, which is in good agreement with the calculated value for 16·5° after allowing for the fact that rotations are always slightly lower at high than at low temperatures (allowing of course for change of density).

Molecular rotation for ethyl acetone-		
dicarboxylate at	16·5° C	9·604
and at	94·0° C	9·374
Difference	77·5°	0·230

or the difference calculated for 100° is 0·297.

This would point to some change taking place in the substance, and as will be seen later, indicates that any enolic tautomer present changes, when heated, into the ketonic compound, so that at 94°, and perhaps also at lower temperatures, it is a pure ketonic substance, but at ordinary room temperatures contains a small quantity of the enolic or unsaturated phase.

10. ISOMERIC COMPOUNDS

It is found that depending upon the nature and type of the compound there is a real difference in the value of M for isomeric substances; thus:

	M	Δ
Propaldehyde	3·332	0·182
Acetone	3·514	
Trimethylcarbinol	5·122	0·345
Ethyl ether	4·777	
o-xylene	13·345	0·486
m-xylene	12·859	0·049
p-xylene	12·810	0·604
Ethyl benzene	13·414	

The 'trans' modification in geometric isomers has generally a higher value of M than the 'cis':

Ethyl maleate (cis)	9·625	Ethyl citraconate (cis)	10·517
Ethyl fumarate (trans)	10·112	Ethyl mesaconate (trans)	11·233

Optically active isomers also show differences in the value of M.

Glucose . .	6·723	Dipentene . .	11·315
Galactose . .	6·887	*d*-Limonene .	11·246
Lactose . .	12·714	Ethyl tartrate .	8·766
Maltose . .	12·690	Ethyl racemate .	8·759

11. CONSTANTS FOR THE ELEMENTS

It is possible to deduce the values for the elements from the values of various series constants. Thus the series constant for paraffins, equal to 0·508, is equivalent of H_2; from which H=0·254 and the value for C=(1·023−0·508)=0·515.

In this manner the values for halogens can be determined from the series constants for alkyl halides, for oxygen in hydroxyl from alcohols, for ketonic oxygen from aldehydes and ketones, etc. The following values are generally employed:

ement	Constant	Element	Constant
H . . .	0·254	Cl . .	1·734
C . . .	0·515	Br . .	3·560
O (OH) . .	0·191	I . .	7·757
O (aldehydes) .	0·261	N . .	0·717
O (ketones) . .	0·375		

12. CONSTANTS FOR THE DOUBLE AND TRIPLE BONDS

The effect of a double bond is, in general, to raise the rotation, for example:

	M	Δ
Ethyl crotonate, $CH_3.CH : CH.CO_2C_2H_5$	7·589	1·112
Ethyl butyrate, $C_3H_7.COOC_2H_5$ . .	6·477	
Allyl alcohol, $CH_2 : CH.CH_2OH$ . .	4·682	0·914
Propyl alcohol, $CH_3.CH_2.CH_2OH$ . .	3·768	
Trimethylethylene, $(CH_3)_2C : CHCH_3$.	6·208	0·578
Pentane, C_5H_{12}	5·630	
Octylene, C_8H_{16}	9·432	0·740
Octane, C_8H_{18}	8·692	

For unsaturated and saturated alcohols and esters of the aliphatic series, Perkin assigns a mean value of 1·112 for Δ.

Different values are obtained in the aromatic compounds, particularly if the double bond forms a part of the ring:

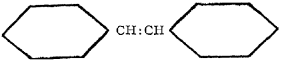
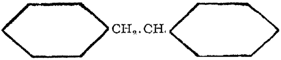
	M	
Cyclohexane . .	5·664	0·728
Tetrahydrobenzene .	6·392	

The value of *Δ* shows a considerable increase if the double bond is in the side chain and a still greater increase if two benzene nuclei are present.

(i)

	M	Δ
Styrene, $C_6H_5CH : CH_2$ . . .	16·041	2·627
Ethyl benzene, $C_6H_5.C_2H_5$ . . .	13·414	
Propenyl benzene, $C_6H_5CH : CH.CH_3$.	17·599	3·046
Propyl benzene, $C_6H_5C_3H_7$ . . .	14·553	
Butenyl benzene, $C_6H_5CH : C(CH_3)_2$.	18·362	2·732
Butyl benzene, $C_6H_5.C_4H_9$ . . .	15·630	
	Mean	2·834

(ii)

		M	Δ
Stilbene		33·143	8·146
Dibenzyl		24·997	

It is interesting to notice that if the double bond in the side-chain is situated still further from the nucleus, the value of *Δ* falls and returns almost to the value for aliphatic compounds.

(i)

	M	Δ
Isoeugenol, $CH_3O.C_6H_3(OH)CH : CH.CH_3$	21·469	2·742
Eugenol, $CH_3O.C_6H_3(OH)CH_2.CH : CH_2$.	18·727	

(ii)

Allyl benzoate, $C_6H_5CO.OCH_2.CH\ \ CH_2$.	15·722	0·849
Propyl benzoate, $C_6H_5CO.OC_3H_7$.	14·873	

(iii)

Allyl phenyl ether, $C_6H_5O.CH_2.CH : CH_2$.	17·134	0·947
Propyl phenyl ether, $C_6H_5O.C_3H_7$ . .	16·187	

The triple bond shows a smaller increase in rotation than the double bond and Δ varies between 0·629 and 0·859.

13. Ring Formation

In 1902, Perkin[28] investigated the effect of ring formation on magnetic rotation and his results may be seen from the following examples:

	M	Δ	Calculated for—	M	
Butyric acid, $C_4H_8O_2$	4·472		Formic acid $+3CH_2$	4·740	
Cyclopropane carboxylic acid, $C_4H_6O_2$	4·141	−0·331	. .	4·141	−0·599
Valeric acid, $C_5H_{10}O_2$	5·513		Acetic acid $+3CH_2$	5·594	
Cyclobutane carboxylic acid, $C_5H_8O_2$	5·048	−0·465	. .	5·048	−0·546
Caproic acid, $C_6H_{12}O_2$	6·530		Propionic acid $+3CH_2$	6·531	
Cyclopentane carboxylic acid, $C_6H_{10}O_2$	5·891	−0·639	. .	5·891	−0·640
Caprylic acid, $C_8H_{16}O_2$	8·580				
Methyl cyclohexane carboxylic acid, $C_8H_{14}O_2$	7·975	−0·605	Valeric acid $+3CH_2$	8·582 7·975	−0·607

Perkin assigns the value 0·6 for ring formation with loss of H_2, but this value is a little higher in hydrocarbons and a little lower in dichlorocyclo-paraffins.

14. Application to Structural Problems

Two cases of classical importance in structural chemistry which have been definitely helped by magnetic rotation measurements are those of the keto-enol tautomerism and the structure of cyclic compounds of the terpene series. The first problem has been easily solved by comparing the calculated values for the enol and keto forms with the observed values for the pure substance. The structure of acetoacetic ester as determined in this way has been found to be entirely ketonic (cf. Sec. 9), while in the case of acetyl acetone, which is a mixture at ordinary temperature of the two forms, there was a definite increase in the keto form at about 93° C.

Structure in the Terpene and Camphor Groups

The rotation for camphor may be calculated as follows:

	M
Methyl hexyl ketone	8·509
$CH_2 \times 2$	2·046
Double ring 0·6 × 2	−1·200
Camphor (calculated)	9·355
Camphor (observed)	9·265

Limonene gives the following result:

Paraffin $C_{10}H_{22}$ (calculated)	10·738
Less ring formation (hydrocarbon)	0·982
	9·756
Unsaturation	1·440
Hence, $C_{10}H_{16}$ (calculated)	11·196
$C_{10}H_{16}$ (observed)	11·204

The difference in structure between bornyl chloride and pinene hydrochloride is very clearly brought out by this method. If the two were identical, the calculated value should agree with that of pinene with the addition of HCl, 0·254+1·734=1·988 minus the value of an ethylenic linkage (0·720). The value of bornyl chloride can then be calculated as follows:

	M
Pinene (observed)	10·294
HCl	1·988
	12·282
Less	−0·720
Bornyl chloride (calculated)	11·562
Bornyl chloride (observed)	11·058
Difference	0·504

Consequently, bornyl chloride must be differently constituted from pinene hydrochloride, as we know it to be on other evidence. If, on the other hand, it has a similar structure to borneol, its value will be that of borneol in which hydroxyl is replaced by chlorine. In passing from secondary octyl alcohol to octyl chloride there is a rise of 1·244 units. If the value is the same when borneol becomes bornyl chloride we have:

	M
Borneol (observed)	9·806
Substituting OH by Cl	1·244
Calculated	11·050
Observed	11·058

15. MAGNETO-ROTATORY EXALTATION

A very interesting observation was made by Perkin[29] in ascertaining the magnetic rotation of the synthetic members of the terpene series. A comparison of two active menthadienes which are structurally closely related reveals a difference in rotation which can only be due to reinforcement produced by the conjugated linkages similar to that observed in the case of refractive exaltation.

	M
p-menthadiene	13·061
p-menthadiene (limonene) . . .	11·246
Difference . .	1·815

The discovery has thrown a new light on certain anomalous results connected with benzene and its derivatives.

16. AROMATIC COMPOUNDS

Perkin found that hexylene and diallyl give normal values, but there is a rise of 3·776 units with the introduction of the third double bond in hexatriene.

	M	Δ
Hexane, $C_6H_{14}CH_3(CH_2)_4CH_3$	6·670	
Hexylene, $C_6H_{12}CH_3(CH_2)_2CH : CH.CH_3$.	7·473	0·803
Diallyl, $C_6H_{10}CH_2 : CH(CH_2)_2CH : CH_2$ . .	8·420	0·947
Hexatriene, $C_6H_8CH_2 : CH.CH : CH.CH : CH_2$	12·196	3·776

A large number of other organic substances have been similarly treated by Perkin, and the reader is referred to his classical memoirs in the *Journal of the Chemical Society, London*, from 1885 to 1907.

17. INORGANIC COMPOUNDS

The magnetic rotatory power of inorganic salt solutions has been widely studied by Schonrock[30], Forchheimer[31], Oppenheimer[32], and a host of other workers. The earliest observations were made with hydrochloric acid and hydrobromic acid by Perkin[33], who showed that the rotations of these acids in non-ionising media such as amyl ether are equal to the sum of the ordinary rotatory effects of hydrogen and halogen, whereas in water they have a different rotatory power which on dilution changes continuously till a constant value is reached. Ostwald[34] thought that this behaviour was in accord with the ionic theory. Later work, however, showed great anomalies, and it was found that salts in general could be divided into three types, (i) those in which molecular rotation is increased with dilution; (ii) those in which rotation decreases with dilution; (iii) those in which it remains constant.

HCl, LiCl, Li_2SO_4, NH_4I constitute examples of (i); Na_2SO_4, H_2SO_4, $LiNO_3$, HNO_3 of (ii); and acetic acid, NaCl, $MgSO_4$, $CdBr_2$, CdI_2 and KCl of (iii).

In the case of formates and acetates the rotation is mostly additive in nature.

It is clear from the data given in this chapter and from the work of Perkin that the applications of this property to structural problems are many, and are limited only by the many errors which may be committed in obtaining theoretical results with a property which is so sensitive to constitutional change. With higher fields and better technique now available, these errors can be minimised. It is by a deeper and more accurate study of this property in relation to constitution that any notable advance can be made.

18. Optical Activity and Magneto-optical Rotation

The property of magnetic rotation seems to be analogous to optical activity inherently present in certain substances like turpentine, tartaric acid, nicotine, etc. One essential difference is that in the former case the absolute direction in which the plane of polarisation is turned is independent of whether the light is passing from the north pole towards the south or from the south pole towards the north; i.e., reflecting the light back on the original path doubles the effect instead of nullifying it as in the case of optical activity. An attempt was made by Bhatnagar, K. N. Mathur and Jain[23] to find out, if possible, any relationship between the magnetic fields required to nullify the optical rotation of an active substance dissolved in a solvent and the fields which will be required to produce the same amount of rotation in the pure solvent itself. Their conclusions were:

(i) That for any particular solvent the current, and hence the field required to just balance the optical rotation, is proportional to the optical rotation itself. That is, if I be the current and θ the optical rotation, then $I \propto \theta$, or since the strength of the field H is proportional to I, $H = K\theta$, where K is a constant. For optically active solutions of solids the value of K is constant for each solvent.

(ii) That unlike optical rotation the magnetic rotation of an optically active solution of a substance is independent of the concentration within the range studied.

This result is of considerable interest from the point of view that very small changes in the amounts of optically active substances produce considerable variation in optical rotation. From analogy it was naturally expected that small changes in their concentration should also produce a corresponding change in magnetic rotation. Thus, for example, for a solution of menthol in benzene when the concentration changes from 0 to 2·90 per cent. the change in optical rotation is from 0° to 2·62°, whereas the magnetic rotation remains unaffected.

(iii) That in the case of solutions of optically active liquids in inactive liquids, where high concentrations of optically active substances could be taken, the magnetic rotation changes with the concentration. It seems to depend upon the volume concentration of each of the liquids. This accords with the conclusions arrived at by Perkin [35] and by Schwers [36], but is at variance with the conclusions reached by Calcagni.[37]

19. THE TIME LAG OF THE FARADAY EFFECT BEHIND THE MAGNETIC FIELD

A magneto-optic method for the chemical analysis of mixtures of compounds, elements and isotopes in solution based on the determination of the differences in the time lag of the Faraday effect behind the magnetic field for the various substances has been suggested by Allison, Beam and Murphy [38], the experimental arrangement of which is shown in Fig. 46.

The parallel plate condenser C, the capacity of which could be varied from 0·0005 to 0·005 mfd., is charged from the high-voltage side of the transformer M, provided with a Kenetron tube rectifier K. The sliding rheostats R_1 and R_2 are in series with the primary of the main transformer and the filament transformer, respectively. Light from a variable spark-gap A is rendered parallel by a converging lens L. F is a colour filter to transmit monochromatic light only. N_1 and N_2 are nicol prisms. B_1 and B_2 are cylindrical glass cells, each wound with a helix of copper wire in an identical manner but opposite in direction. B_2 is capable of being moved in the direction AN_1N_2 without disturbing the rest of the arrangement. T_1T_1 and T_2T_2 are two sliding trolleys. A shift in the position of the trolleys, effected by a hand-wheel mechanism, brings about a change in the length of the circuits $PT_1B_1T_1P$ and $PT_2B_2T_2P$.

If now, the divided circuits are such that equal and symmetrical impulses, originating from the spark-gap A, pass through them, we shall have in the cells B_1 and B_2 magnetic fields equal in magnitude but opposite in direction at every instant of the growth and decay of an electric impulse. When this is the condition, the magnetic rotation, for any liquid, in one cell is exactly neutralised by that in the other.

To begin with, B_1 and B_2 are removed and the nicol prisms N_1 and N_2 are crossed. B_1 and B_2 are then filled with the same liquid and placed in position. Trolleys T_1T_1 and T_2T_2 are moved back and forth till at a certain point light is completely extinguished to an observer at E. At this point the magnetic rotation in one is annulled by that in the other, and also the magnetic field in B_2 is behind the field in B_1, by a time equal to that taken by light to travel from the centre of B_1 to that of B_2.

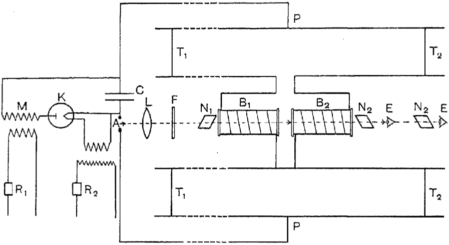


FIG. 46.—Allison's apparatus for studying time-lag of Faraday effect.

The liquid in B_2 is then replaced by the liquid in question, all other arrangement remaining unchanged. Light now passes through the nicol N_2, but, if B_2 be moved backwards along AN_1N_2, a position is found where minimum of light passes through N_2. If *d* be the distance through which B_2 is moved to get this position and *c* be the velocity of light, then for the particular wavelength Faraday effect lags behind the magnetic field longer in the second than in the first liquid by an interval d/c seconds.

In the foregoing method, determinations of the time-lag difference have been made by keeping the trolleys fixed and moving the cell B_2. But results of the same accuracy could be obtained by keeping B_2 fixed and moving one of the trolleys T_1T_1 and T_2T_2 till the minimum appears.

The time constant of the electric impulses was determined by the capacity of the condenser, but no high-frequency electrical oscillations large enough to affect B_1 and B_2 after the initial discharge, could be detected experimentally. This was tested in several ways.

A test coil attached to a vacuum thermocouple and placed alternately in the helix of B_1 and B_2 or a thermo-galvanometer connected in series with one branch of the circuit, indicated no maximum or minimum readings corresponding to different points of the scale as the trolley was displaced. A vacuum tube oscillator, also, gave no indication of any oscillation.

Tests were made to see if the retardation exerted by different liquids in the tubes B_1 and B_2 upon the flow of the electric impulses through the divided circuits could account for the lag of the Faraday effect.

Small differences in temperature were found to have no effect on the Faraday lag.

In studying solutions of different substances it was found that each substance, regardless of the presence of other substances, produced the characteristic minimum of light intensity, which persisted until the concentration was reduced to about 1 part in 10^{11}.

After studying a number of substances it was concluded that positions of the minima were functions of the atomic weights, or more precisely of chemical equivalents of elements. This method, therefore, was applied to the investigation of the isotopes of Au, Pt, Rb, Ru, Ta, Th and of element 85, and to the discovery of element 87 from the study of the solutions of the minerals pollucite and lepidolite (cf. Chapter XIV, Section 3). The claims of these investigators are, however, still open to controversy because both mass spectrograph and X-ray examination of the preparations, supposed to contain large quantities of element 87 by magneto-optic method, did not indicate the presence of this element. The existence of six isotopes of an element of odd atomic number, like 85, as shown by magneto-optic method, appears also somewhat unlikely.

II. *The Magnetic Double Refraction or the Cotton-Mouton Effect*

Faraday, after the discovery of the magnetic rotation of the plane of polarisation, sought for the effect of magnetic field on a beam of light propagated in a direction perpendicular to the lines of magnetic force but without success. The quest was, however, intensified by the discovery of the Kerr effect. On the analogy of Kerr's discovery[39], Majorana[40] sought for birefringence in a mobile magnetic medium placed in a magnetic field. He found that to a slight extent in a solution of ferric chloride, and notably in some kinds of dialysed iron and ferric oxide in colloidal solution, the plane polarised light was converted into a circularly polarised light when such solutions were subjected to a constant magnetic field. Voigt[41] and Zeeman and Geest[42] also made similar observations. Majorana[40], however, did not find any effect in pure liquids.

In 1907 Cotton and Mouton[43], the celebrated French scientists, observed for the first time an effect quite distinct from the Faraday effect. They found that when light traverses a pure liquid placed in a strong magnetic field in a direction transverse to the lines of force, as against parallel in the case of the Faraday effect, the liquid exhibits a feeble birefringence. This effect was first noticed by them in a liquid in which it is specially conspicuous, namely nitrobenzene, but they soon verified the phenomenon in the case of a large number of other liquids, particularly of the aromatic series. With stronger magnetic fields they were able to measure the birefringence in the case of a large number of aliphatic liquids also. With the aid of their first arrangement, however, they were unable to measure the birefringence in the case of such liquids as water, alcohols, acids and hydrocarbons which are considerably employed as solvents. Ramanadham[44] has recently devised an experimental technique which has enabled him to measure the birefringence in these cases. Also Haque[45], working on the Cotton Magnet in Sorbonne, has determined the values of birefringence for water, alcohols and nitrate solutions. Further work on magnetic birefringence in aliphatic liquids has been done by Chinchalkar[46] using a half-shade compensator of strained glass, and also by Scherer.[47]

A brief account of the experimental arrangement employed by Ramanadham is given in the next section.

20. THE EXPERIMENTAL TECHNIQUE OF RAMANADHAM

The experimental arrangement consists of a strong beam of light from a point source of light which is rendered parallel by means of a condensing lens and a collimating lens provided with a collimating tube and a slit. It is plane-polarised in a plane inclined at 45° to the vertical by a nicol. The polarised light after passing through the experimental tube is extinguished by means of another nicol followed by a Rayleigh compensator, whose description will follow later. In the telescope, placed next to the compensator, a dark band is seen in the middle of a white patch of light due to the use of the compensator. When the magnetic field is on and in the absence of the compensator, there should be a restoration of light in the second nicol, which if due to genuine double refraction cannot be quenched by rotating it. Such restoration of light can be readily seen in the case of benzene and other aromatic liquids. In the case of the aliphatic compounds, the restoration of light is so feeble that one might easily mistake an uneliminated Faraday effect (about which more will be said in what follows) for the double refraction. In such cases, the compensator with the aid of the telescope will give indications of the double refraction by a motion of the dark band upwards or downwards.

A very large electromagnet constructed under the supervision of Sir C. V. Raman[48] was used for Ramanadham's experiments. It had pole-pieces of specially designed form which were cast, machined and fitted to the faces of the field magnet of an old dynamo. The pole-pieces concentrate a strong field in a gap 33 cm. long, 1 cm. broad and 1 cm. high, the length of the gap being transverse to the lines of force. This great length and small cross-section of the gap was an advantage, as the difference of phase between the components of the doubly refracting beam is proportional to the length of the path of the light in the doubly refracting medium. In the expression for the Cotton-Mouton constant, namely

$$C_m = \frac{n_p - n_s}{\lambda H^2}$$

it is seen that the double refraction is proportional to the square of the magnetic field. Thus, a strong field and a long path in it were advantageous to the detection and measurement of feeble birefringence. The average field strength was 21,000 gauss.

If the beam of light does not cut the lines of force exactly at right angles, it is possible that the strong fields used for the experiment may have an effective component in the direction of the beam. This may give rise to a Faraday effect, and therefore we may get restoration of light due to Faraday effect also. It is therefore essential to see that the beam of light should be as nearly as possible perpendicular to the lines of force. In view of this, the following precautions taken will be readily understood.

By means of the collimating and condensing lenses an almost perfectly parallel beam of light was obtained. In addition to this it was made accurately co-axial with the length of the gap. For this purpose, the heights of the collimating lens, the condensing lens and the source of light were carefully adjusted.

The experimental tube was made of Jena glass and was perfectly straight. The ends were ground perpendicular to the length of the tube, so that when the cover-slips were pasted on to them they would not form a wedge and thus cause the deviation of light from its right path.

The use of a Rayleigh compensator[49] served the double purpose of detecting feeble double refraction and of ascertaining the elimination of the Faraday effect. Its principle is as follows: A flint glass is bent in a vertical plane, by supporting it by its ends in a suitable clamp and applying a small adjustable force at its centre. The glass thus strained is interposed between the crossed nicols, so that the light emerging from the experimental tube passes through it to the analysing nicol. The double refraction induced in the glass plate manifests itself by the restoration of light in the field everywhere except along a horizontal dark band which corresponds to the neutral axis of the plate. If any doubly-refracting medium is interposed between the strained glass and the polariser, there will be a shift of the dark band which can be readily observed with reference to the crosswire in the telescope. This shift will occur to an extent such that the double refraction of the strained glass at the new position of the band is equal and opposite to the superimposed double refraction.

21. POSITIVE AND NEGATIVE MAGNETIC BIREFRINGENCE

There are two kinds of magnetic birefringence, according as the shift of the dark band is upwards or downwards (downwards or upwards as seen in the telescope). The former is called the negative double refraction and the latter positive. In the former, the light vibrations perpendicular to the lines of force have a greater refractive index than those which take place along the lines of force. In the latter the reverse is the case.

In order to quantitatively estimate both kinds of double refraction, the method adopted was to compensate the shift by interposing another glass plate and compressing it either

TABLE III

COTTON-MOUTON CONSTANTS FOR COMMON SUBSTANCES

Liquid examined	Relative Value of C_m corresponding to Nitrobenzene = 100	Absolute Value of $C_m \times 10^{14}$	Liquid examined	Relative Value of C_m corresponding to Nitrobenzene = 100	Absolute Value of $C_m \times 10^{14}$
Pentane	-0·7	-1·8	Allyl alcohol	1·1	2·7
Heptane	-1·0	-2·5	Methyl cyanide	-1·3	-3·3
Octane	-1·2	-3·0	Ethyl sulphide	-0·8	-1·6
Nitromethane	3·6	9·1	CH_3-CHCl_2	-1·8	-4·6
Tetranitro-			CH_2Cl		
methane	1·0	2·5	$\vert$	-2·1	-5·3
Chloropicrin	3·4	8·8	CH_2Cl		
Isoprene	2·7	6·8	Bromoform	-6·8	-17·2
Chloroform	-2·8	-7·0	$CH_2.Br$		
Water	-0·4	-1·1	$\vert$	-7·1	-18·0
Methyl alcohol	-0·7	-1·8	$CH_2.Br$		
Ethyl alcohol	-0·4	-1·1	Ethyl tribrom-		
Propyl alcohol	-0·4	-1·1	acetate	-2·2	-5·6
Butyl alcohol	-0·9	-2·2	Methyl iodide	-2·9	-7·3
Ethyl ether	-0·9	-2·2	$CH_2.I_2$	-12·3	-31·1
Acetone	1·6	4·1	Carbon disulphide	-19·6	-49·6
Diethyl ketone	1·1	2·7	$S=C=NC_2H_5$	-8·4	-21·3
Methyl ethyl			Iso-amylene	2·6	6·8
ketone	1·1	2·7	Formamide	1·2	3·1
Methyl propyl			Ethyl formate	0·3	0·7
ketone	1·1	2·7	Propyl formate	1·1	2·7
Acetyl acetone	4·2	10·6	Ethyl acetate	0·4	1·0
Formic acid	2·5	6·5	Propyl acetate	0·5	1·4
Acetic acid	1·1	2·7	Carbon tetra-		
Propionic acid	1·1	2·7	chloride		
Butyric acid	0·7	1·8	Trimethylamine	Undetectable	
Caproic acid	0·7	1·8	Isopropyl alcohol		
Heptoic acid	0·5	1·4	Iso-butyl alcohol		
Caprylic acid	Undetectable		Glycerol	-2·0	-5·1

horizontally (for the positive birefringence) or in a vertical direction for the negative birefringence.

The relative and absolute values of the Cotton-Mouton constant for some more common substances are shown in Table III.

22. MAGNETIC DOUBLE REFRACTION AND CHEMICAL CONSTITUTION

It is clear from the results that the property of magnetic double refraction is very sensitive to changes of molecular structure. It has been already pointed out that the benzene and naphthalene series manifest a considerable double refraction. The results of Cotton and his pupils have established that in the case of mono-substituted derivatives of benzene, some substituents increase the specific birefringence, while others decrease it. Those groups which enhance the value of double refraction are of the type $—NO_2$, $—C{\equiv}N$, $—C{\equiv}CH$, $—CH_3$. The groups which decrease the value are of the type NH_2, OC_2H_5, C_3H_7, Br, F, Cl, I.

Regarding aliphatic substances the following general conclusions have been arrived at:

(i) All saturated aliphatic compounds such as hydrocarbons, alcohols and several other derivatives of hydrocarbons show negative birefringence.

(ii) Water and alcohols show negative double refraction.

(iii) Glycerol and substances with three hydroxyl groups show considerably greater double refraction than the monohydroxy alcohols.

(iv) Allyl alcohol and α-isoamylene show in a remarkable manner the influence of the addition of unsaturated bonds due to which there is a reversal from negative to positive double refraction.

(v) Compounds containing the carbonyl group show positive birefringence, for example, ketones, fatty acids and their esters.

(vi) From the results that ethyl ether and the alcohols show negative birefringence while compounds containing carbonyl groups show the reverse, it is probable that oxygen plays a different rôle in the alcohols, ethers and in the ketones. This result is in line with Pascal's observations on magnetic susceptibilities.

The work published on magnetic double refraction shows clearly how this property is capable of being utilised by the chemist for the determination of chemical constitution and for getting reliable final evidence in favour of one structural formula or another. The significance of this enquiry has been enhanced by the work of Raman and Krishnan[50] and Ramanadham[44] on the theoretical and practical aspect of magnetic double refraction.

23. BIREFRINGENCE IN PARAMAGNETIC SALTS

The magnetic birefringence in pure liquids and solutions had so far been observed in diamagnetics only, the only exception being an observation by Elias[51] on a solution of erbium nitrate, which, however, had attracted very little attention. Interest in paramagnetic birefringence has been enhanced by Chinchalkar's work[52] on magnetic birefringence in paramagnetic salts of rare earths.

24. THEORY OF MAGNETIC DOUBLE REFRACTION—LANGEVIN

Langevin[53] explains magnetic double refraction as an effect arising from the orientative action of the field on the molecules assumed to be magnetically and optically anisotropic. He connects the absolute value of the Cotton-Mouton constant with the values of the optical refractivity and of the magnetic susceptibility of the molecule along the three mutually perpendicular axes. According to this theory the Cotton-Mouton constant denoted by C_m is given by the relation, omitting paramagnetic terms,

$$C_m=\frac{n_p-n_s}{\lambda H^2}$$

$$\frac{3(n_0^2-1)^2}{80\pi n_0\lambda kTN_v}\,\frac{[(A-B)(A'-B')+(B-C)(B'-C')+(C-A)(C'-A')]}{(A+B+C)^2} \quad . \quad . \quad (1)$$

where A, B, C are the moments induced along the three mutually perpendicular axes of the optical ellipsoid of the molecules, by unit electric force in the incident light-waves acting respectively along the three axes. The quantities A, B, C are connected with the refractive index n_0 of the liquid by the relation

$$A+B+C \quad \frac{3}{4\pi N_v}\cdot\frac{n_0^2-1}{n_0^2+2} \quad . \quad . \quad . \quad (2)$$

A′, B′, C′ are the magnetic moments induced in the molecule by unit magnetic force acting in the same three directions, and the quantities A′, B′, C′ are connected with the magnetic susceptibility of the medium by the relation

$$\frac{A'+B'+C'}{3}=\frac{\chi_v}{N_v} \quad . \quad . \quad . \quad (3)$$

where χ_v is the susceptibility per unit volume. H is the magnetic field, λ the wavelength of the light, k the Boltzmann constant, T the absolute temperature, N_v the number of molecules per unit volume, n_0 the refractive index of the liquid outside the field and n_p and n_s are the principal refractive indices in the field.

It is easily seen from equations (1), (2) and (3) that the Cotton-Mouton constant depends essentially on the difference of the magnetic susceptibilities of the molecules along the three directions which form the axes of the optical ellipsoid of the molecule.

An interesting application of this theory in the case of crystals has been made by Raman and Krishnan. This will be dealt with in a later chapter on magnecrystallic action.

III. *The Kerr Effect*

Kerr[39] investigated the influence of a powerful magnetic field on the state of polarisation of light when reflected from a polished pole of an electromagnet. It is well known that plane polarised light reflected from a polished surface is elliptically polarised and the reflected beam cannot be extinguished by the analyser. If, however, the incident beam is plane-polarised at right-angles to or in the plane of incidence, the reflected beam is simply plane-polarised and can be then extinguished by means of another nicol. Kerr adopted the second arrangement and showed that when the electromagnet was excited, the reflected light was no longer plane-polarised but developed elliptical polarisation. The two arrangements employed by Kerr are shown in Figs. 47 and 48.

N and S refer to the poles of the electromagnet; P to the polariser and B to the analyser, S′ is the source of light and R the reflecting glass. The results obtained by Kerr are as follows:

(i) When the light is polarised in the plane of incidence, the magnetic rotation is negative for all angles of incidence.

(ii) When the light is polarised normally to the plane of incidence, the rotation is negative for all incident angles between 90° and 75°.

(iii) The magnetic rotation referred to under (ii) disappears altogether at 75° and reappears with a positive sign for all angles between 75° and 0°.

(iv) There is no magneto-optical effect when the wave-front is parallel to the lines of force.

(v) The rotation of the polarised ray is proportional to the intensity of magnetisation, i.e. $\theta = KI$ (where K is the Kerr constant).

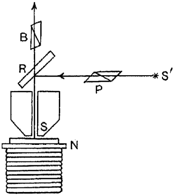


FIG. 47.—Kerr effect at normal incidence.

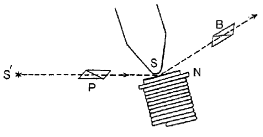


FIG. 48.—Kerr effect at different angles.

Kundt[54] examined these results and came to the conclusion that all these effects can be satisfactorily explained by assuming that when light strikes a reflecting surface it penetrates to some depth and the rotation observed is really nothing else but a Faraday effect in a thin film.

This effect deserves more careful and extensive study, particularly in paramagnetic solutions placed in cavities in the pole-pieces of the electromagnet, and if the conclusions arrived at by Kundt are correct it should become a powerful method for determining the composition and constitution of thin films and the orientation of molecules at the surface of the liquids.

IV. *The Photomagnetic Effect*

Considerable interest has been aroused by the recent announcement of Bose and Raha[55] that, on exposure to light, chromic chloride and several other salts show a decrease in their paramagnetic susceptibility. Later experiments of these authors showed that a mistake with respect to the sign of the change led to erroneous conclusions, and that the previously observed decrease was really a slight increase in the majority of cases examined by them.

Specchia[56], Gorter[57] and Selwood[58] have also investigated this phenomenon, and their conclusions are as follows:

(*a*) Specchia finds a slight increase followed by a slow decrease.

(*b*) Gorter finds that there is no increase whatsoever, but that there is a decrease which he attributes to the slight rise in temperature when the substance is exposed to light.

(*c*) Selwood, employing an apparatus used by Decker[59], confirms the results of Gorter and is unable to detect the photomagnetic effect.

Bose and Raha[60] have suggested a theoretical reason for the alleged effect. According to them, light causes a temporary breakdown of the L coupling between the paramagnetic ion and the associated solvent molecule, thereby reducing the damping of the orbital moment (cf. Chapter IX, Section 12). Selwood raises the objection that this mechanism cannot explain why the magnitude of the increase in χ is the same both in the didymium salts and ferric chloride. In didymium salts $4f$ electrons are responsible for the paramagnetism. These electrons are completely secured from external influences by the completed shells on either side of them, while for elements of the iron group the orbital moments are usually strongly damped by the electrons of neighbouring ions or molecules. Similarity of behaviour is thus a very doubtful proposition in the two cases.

The photomagnetic effect is still a controversial question and further research is needed on the subject.

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CHAPTER XI

SOME IMPORTANT MAGNETIC EFFECTS

THERE are a number of magnetic phenomena, such as magnetostriction, the Barkhausen, the Hall and the thermomagnetic effects, which at the present moment seem to have no direct bearing upon magnetochemistry. Since these phenomena are influenced by the presence of materials which modify their physico-chemical properties, the problem will become more and more chemical as we approach nearer and nearer the ultimate cause of these phenomena. Ultimately it is hoped that they will help in understanding the nature of the elementary magnet and the theory of atomic structure, which are the two most outstanding problems of magnetochemistry. Some of these effects have assumed importance also on account of their significance in applied physics and chemistry and in engineering. We shall deal briefly with these effects and shall begin with the magneto-mechanical effects, namely, (*a*) mechanical effects due to magnetic fields, and (*b*) magnetic changes due to mechanical stresses.

(*a*) Mechanical effects due to magnetic fields may include:

(i) *Joule Effect.*—Change in length due to a longitudinal magnetic field.

(ii) *Transverse Joule Effect.*—Change in dimensions in direction normal to the magnetic field.

(iii) *Changes in Young's modulus due to magnetisation.*

(iv) *Guillemin Effect.*—Bending due to a magnetic field.

(v) *Wiedemann Effect.*—Circular changes: twist due to the interaction of circular and longitudinal fields.

(vi) *Change in the coefficient of rigidity due to a magnetic field.*

(vii) *Barrett Effect.*—Change in volume due to magnetic field.

(*b*) Magnetic changes due to mechanical stresses may include:

(i) *Villari Effect.*—Change in induction due to longitudinal stress.

(ii) *Transverse Villari Effect.*—Change in induction due to transverse stresses.

(iii) *The Werthiem Effect.*—Circular magnetisation due to twisting a longitudinally magnetised rod.

(iv) *Nagaoka-Honda Effect.*—Change in intensity of magnetisation due to volume changes.

Besides these effects the gyromagnetic effects (namely effects which show that magnetisation may be accompanied by rotation and rotation by magnetisation) have been responsible for a lot of very painstaking investigations on the subject of magnetism.

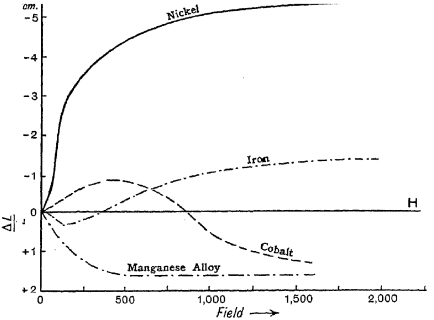

FIG. 49.—Influence of magnetic fields on the ratio $\frac{\Delta L}{L}$ for some ferromagnetics (Joule effect).

I. JOULE EFFECT

Amongst the effects described in (*a*) the most important are the Joule effects,[1] both linear and transverse. If an iron rod is introduced in a solenoid carrying an electric current, the rod becomes magnetised longitudinally and a change in length is observed. This change is a very small one and its accurate measurement is possible only by means of sensitive instruments like the extensometers or the Newton ring and interferometric methods, or by means of ultra-micrometers. For practical details the reader is referred to Williams' book on *Magnetic Phenomena.*[2]

When studied under various conditions the Joule effect shows that it is very sensitive to the environments, for example, the temperature and pressure. The curves in figure (49) illustrate the influence of magnetic fields on lengths in the case of iron, nickel and cobalt and an alloy of manganese. Iron shows an increase in length for weak fields and decrease for strong fields. Nickel exhibits a shortening for all field strengths and the Heusler alloy shows on the other hand an increase in length for all field strengths. Cast cobalt behaves in a manner just opposite to that of iron, decreasing in length for weak fields and increasing for strong ones.

An interesting new line of study is the investigation of these effects in single crystals. The work of Heaps [3] on magnetite and that of McKeehan [4] on the theoretical aspect of magnetostriction deserves special study. The chemical impurities which influence the structure and other physical properties have a very definite rôle in the phenomena and require to be carefully investigated.

Simultaneously with changes in lengths a volume change was found to occur in experiments on magnetostriction. This phenomenon is known by the name of the transverse Joule effect.

Joule's first method which led to this discovery was to pass an electric current through an insulated wire wound inside an iron tube. This gave lines of force which were circular and the change in dimensions normal to the field was observed by measuring the change in length of the tube. More accurate measurements on this subject are due to Heaps,[5] Brown,[6] Bidwell [7] and Williams.[8]

2. VILLARI EFFECT

In the converse effect of mechanical stress on the magnetisation the Villari effect is of great interest. It was first discovered by Matteucci [9] that if a rod of iron in the process of magnetisation is stretched its magnetisation is thereby increased. Villari [10] investigated this effect more thoroughly and showed that Matteucci's results hold only if the iron is weakly magnetised. If it is strongly magnetised stretching makes the rod less magnetised. From this it is clear that there must be a certain critical value for the magnetising force such that stretching the rod has no effect on its magnetisation. The problem is already of great interest in engineering, but a further point of interest would be to measure the influence of impurities, both ferro- and diamagnetic, on the nature and magnitude of the Villari effect and to extend these investigations to the para- and ferromagnetic alloys.

The Nagaoka-Honda[11] effect is also of similar interest. But the most important from our point of view is, however, the gyromagnetic effect, which we shall take up in some detail.

3. THE GYROMAGNETIC EFFECT

The process of magnetisation of a suspended wire of a ferromagnetic substance involves a type of recoil, as we assume the magnetic properties of these substances to originate from elementary magnets or electrons circulating in closed orbits the planes of which in the case of para- and ferromagnetism are oriented by the magnetic field. From this it is obvious that the suspension of the wire should experience a torque as a result of the opposite angular momentum developed in the wire. This and its converse are jointly called the gyromagnetic effect. Important early attempts to detect this effect were due to Maxwell[12] (1861), Perry[13] (1890) and Richardson.[14] They were all unsuccessful in their attempts. The earlier successful attempts are due to Einstein and De Haas[15] (1915) and to S. J. Barnett[16] (1915), and latterly to Chattock and Bates.[17]

Since the magnetic moment depends upon the orbital motion of electrons, it follows that magnetisation should be accompanied by a change in the angular momentum. As shown in Chapter V, Section 15 (eq. 11), the magnetic moment μ is related to the mechanical moment P by the relation

$$\mu = \frac{e}{2mc} \mathrm{P}$$

or

$$\frac{\mu}{\mathrm{P}} = \frac{e}{2mc}$$

where e is the electronic charge, m its mass and c the velocity of light. The calculated value of $\frac{\mu}{\mathrm{P}}$ from the above expression was found to be half of that actually observed in the gyromagnetic experiments and constituted an anomaly which has been responsible for a lot of very elaborate investigations both theoretical and experimental. On the theory of the anomalous Zeeman effect the above expression becomes

$$\frac{\mu}{P}=g\cdot\frac{e}{2mc}$$

where g is the Lande splitting factor.

It is possible to calculate the value of g from the experimentally determined value of gyromagnetic ratio $\frac{\mu}{P}$ and for all ferromagnetic substances it is found that $g=2$. The meaning of this on the modern spectroscopic theory is that the spin of the electron is the cause of ferromagnetism.

The gyromagnetic effect in case of paramagnetics is very difficult to measure as it is not possible to magnetise them strongly. Sucksmith[18] has devised an ingenious method for measuring the gyromagnetic ratio and has studied the substance Dy_2O_3 very carefully.

For Dy^{+++} the theoretical value of g is 1·33 for the state $^6H_{15/2}$ deduced by Hund[19] as being the most probable for this ion. From the gyromagnetic ratio the value of g obtained was 1·36. Further confirmation of the theoretical and experimental values of g has been obtained by Sucksmith[20] in the case of Gd^{+++}, Nd^{+++} and Eu^{+++}. Gd was used in the form of oxide, Gd_2O_3. Hund gives $^8S_{7/2}$ as the ground state for this ion in the gaseous state, there being seven magnetic electrons in the $4f$ shell. With $J=7/2$ the theoretical value of $g=2$ is obtained, since the whole of the moment is assumed to be due to spin; the experimental value is 2·12. For Nd^{+++} Hund gives the ground state to be $^4I_{9/2}$, i.e. $J=9/2$, giving for the theoretical and experimental values for g the values 0·75 and 0·78 respectively. Some experimental difficulties were encountered in the case of Eu^{+++} due to which it was not possible to obtain a very correct estimate of g. The theoretical value is 6·4 and the experiments gave a value $>4{\cdot}5$. The agreement is as good as could be expected under the circumstances.

Thus for paramagnetic materials, experiment and theory yield the important result that the magnetic moment is the resultant of orbital and spin moments. These results yield beautiful confirmation of Van Vleck and Linus Pauling's treatment of paramagnetism.

Some interesting work on ferrites has recently been done by D. P. Ray Choudhry.

It is of interest to note here that the concept of the spinning electron, which has been extraordinarily successful in clearing the theory of spectra, was first suggested (1921) for the gyromagnetic effect (so-called Richardson-Barnett effect) by A. H. Compton [21] in these beautiful words: 'In the first place, the Richardson-Barnett effect shows that magnetism is due chiefly to the circulation of negative electricity whose ratio of charge to mass is not greatly different from that of the electron. In the second place, experiments on the diffraction of the X-rays by magnetic crystals indicate that the elementary magnet is not any group of atoms, such as the chemical molecule, nor even the atom itself, but lead rather to the view that it is the electron rotating about its own axis which is responsible for the ferromagnetism. And finally, positive evidence in favour of the hypothesis of some form of magnetic electron is supplied by a consideration of the curvature of the tracks of β-rays through air. The electron itself, spinning like a tiny gyroscope, is probably the ultimate magnetic particle.'

4. THE GALVANOMAGNETIC AND THERMOMAGNETIC EFFECTS

From amongst other notable magnetic effects, reference must be made here to the influence of magnetic fields on the flow of electric current and heat. These constitute the well-known 'galvanomagnetic' and 'thermomagnetic' effects. The numerous effects described under this head are fully discussed in a monograph on the subject of galvanomagnetic and thermomagnetic effects by Campbell,[2] and the reader is referred to this book for fuller information. It will suffice for our purpose to indicate what they are and to give a brief outline of the more important of these effects, particularly those which are of physico-chemical interest and significance. Most of these effects are correlated, and the following table exhibits in a convenient form the nature of this relationship.

5. THE HALL EFFECT

The most important amongst the galvanomagnetic effects is the Hall effect. In 1878 Hall[22] discovered that when an electric current circulates through a thin plate of metal a magnetic field

TABLE I

THE THERMO- AND GALVANOMAGNETIC EFFECTS (Campbell)

	Thermomagnetic Effects		Galvanomagnetic Effects	
	Thermo-electric	Thermo-thermal	Electro-electric	Electro-thermal
Transverse Effects	Difference of potential: Nernst Effect	Difference of temperature: Righi-Leduc Effect	Difference of potential: Hall Effect	Difference of temperature: Ettingshausen Effect
Longitudinal Effects	Difference of potential	Difference of temperature change in thermal conductivity	Difference of potential change in resistance	Difference of temperature
Allied phenomena	Change in thermo-electric property in magnetic field	Change in temperature in magnetic field	Electro-motive force of magnetisation	Change in Peltier Effect in magnetic field

would rotate the equipotential lines when the field is normal to the lines of flow.

Since then a large volume of experimental work has been done on all sorts of conductors, including metals, gases, electrolytes and colloidal electrolytes, but the behaviour of different substances and of the same substance under different conditions is so complex that the theory of the phenomenon is far from clear. Let C be the current in a plate of width b and thickness d, and H the strength of the magnetic field normal to the current and the width of the plate. The whole of the transverse e.m.f. is proportional to b, H and current density C_i. If R be the coefficient of the Hall effect, the e.m.f. per unit width can be expressed as follows:

$$\frac{E}{b}=RHC_i=RH\frac{C}{b.d}$$

That is,

$$E=\frac{RHC}{d} \quad \text{or} \quad R=\frac{Ed}{CH}$$

The Hall effect may also be considered as a rotation of the equipotential lines through an angle ϕ, given by the expression:

$$\tan\phi=\frac{RH}{r}$$

where r is the specific resistance of the material under investigation.

When the current flows from left to right, R is positive if equipotential lines rotate in the same direction as the current flows in the exciting electromagnet (e.g. in Sb, Zn, Fe, Co), and it is negative if they rotate in the reverse direction as in bismuth, nickel, gold, etc.

6. RICHARDSON'S ELECTRON THEORY OF THE HALL EFFECT

In 1914 Richardson[23] developed a theory for the Hall effect from a consideration of the motion of negatively charged electrons in a state of thermal agitation, and placed under the influence of electric and magnetic forces. The e.m.f. set up by the magnetic field H is given by the equation

$$\mathrm{E}=\frac{2}{3}\,\frac{\mathrm{H}i}{ne}\ \text{(e.m.u.)}$$

in which i is the primary current, n the number of electrons in a unit volume, e the electronic charge. The Hall coefficient would therefore be given by

$$R=\frac{2}{3}\cdot\frac{1}{ne}$$

Since e has a negative sign, this requires all Hall effects to be negative, which, however, is not the case.

Richardson suggested that the positive effect may be due to the polarisation of the electrons in metals setting up an influence in opposition to the external field.

Since the value of e is approximately -10^{-20} e.m.u., that of n of the order of 10^{20} to 10^{24}, R should be of the order 10^{1} to 10^{-4}. The following are some of the values of R for different metals:

Bi	$-10{\cdot}27$	Pb	$+0{\cdot}00009$
Cu	$-0{\cdot}0005$	Fe	$+0{\cdot}0114$
Au	$-0{\cdot}00066$	Sb	$+0{\cdot}22$

The above values of R range from 10^{1} to 10^{-4}, and give a mild support to the theory.

7. THE HALL EFFECT IN ELECTROLYTES AND LIQUID METALS

The Hall effect in electrolytes and in liquid metals has not been satisfactorily established. The careful investigations of Fenninger[24] on solid and liquid mercury have shown that there is practically no Hall effect in liquid mercury. The Hall effect in electrolytes has been investigated by many workers, notably by Roiti[25], Florio[26], Chiavassa[27], Heilbrun[28], Oxley[29], Righi[30] and others. Most of the results are negative, although Van Everdingen[31] and Donnan[32] have established the theoretical possibility of the Hall effect in electrolytes. Donnan has further predicted the conditions under which a positive result may be expected.

8. DONNAN'S THEORY OF THE HALL EFFECT IN ELECTROLYTES

In 1898 Donnan[32] considered the theory of the Hall effect in electrolytes as follows:

Suppose the primary current in the electrolyte flows under an e.m.f. of $\frac{dE}{dx}$ in the direction of the axis of x and that the lines of magnetic force lie along the axis of y, then the Hall difference of potential $\frac{dE_1}{dz}$ would be along the axis of z; and for very dilute solutions it can be shown that

$$\frac{dE_1}{dz}=A\epsilon(v-u)H\frac{dE}{dx}$$

For complete dissociation this expression becomes

$$\frac{dE_1}{dz}=\tfrac{1}{2}A\epsilon(v-u)H\frac{dE}{dx}$$

in which A is the valency of each ion, ϵ the quantity of electricity associated with gm. equivalent of ionic matter, u and v are the respective velocities of the positive and negative ions per unit potential gradient.

Donnan showed that the ratio of the Hall e.m.f. to the primary e.m.f. is approximately of the order 16×10^{-13} for fields ranging from 400 to 1000 gauss.

It would be interesting to measure the Hall effect in fields of, say, up to 50,000 gauss now available in improved electromagnets and with larger potential differences in very dilute solutions of electrolytes. According to Donnan's calculations, if the fall of potential in the cell containing the solution was of the order of 10,000 volts per cm. and a large enough magnetic field could be applied, the effect would become capable of measurements.

A search for the Hall effect in colloidal electrolytes was made by Jain and Kohli[33], but they were unable to obtain any effects up to approximately 17,000 gauss. They, however, noticed that when one Hall electrode was in advance of the other a longitudinal galvanomagnetic effect, reversible with the primary current but not with the magnetic field, was observed.

9. A PECULIAR HALL EFFECT IN CUPROUS OXIDE (KIKOIN-NOSKOV)

Kikoin and Noskov[34] have recently observed a new type of photoelectric effect in cuprous oxide in a magnetic field. When a plate placed in a magnetic field parallel to its plane and immersed in liquid air is exposed to a beam of white light at right angles to its plane an electromotive force E is developed between A and B. The characteristic features of this effect are that—

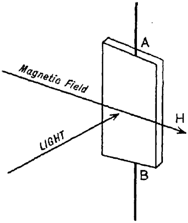

FIG. 50.

(i) E changes its sign with the reversal of the magnetic field although its absolute magnitude remains constant.

(ii) Up to fields of about 2500 gauss E is a linear function of H, the maximum value of E at this field strength being 2·7 volts.

(iii) E reverses in sign when the plate is illuminated from the opposite side without changing the direction of the current in the electromagnet.

(iv) It disappears completely when a source of red light is used.

(v) It disappears at room temperature.

(vi) It is independent of the intensity of light.

Kikoin and Noskov believe that the effect represents a peculiar Hall effect of the moving photo-electrons produced at the entrance of the beam of light into the cuprous oxide. Results of further investigations are awaited with interest.

10. THE ETTINGSHAUSEN EFFECT

Amongst the galvanomagnetic effects this ranks second in importance to the Hall effect. In 1887 Ettingshausen[35] discovered that when a plate of bismuth carrying an electric current was placed in a magnetic field at right angles to the lines of force an unequal change in temperature was observed to be produced at its lateral edges. The arrangement employed by him is shown diagrammatically in Fig. 51.

The letters C, C represent the heavy copper wire soldered to the plate, which is rectangular. Exactly in the middle of the lateral edge are soldered two thermocouples, *t*, *t*, for detecting changes in temperature. On exciting the magnetic field and allowing the current to flow through the plate as shown in Fig. 51A, one of the edges A became cooler while the other B became warmer.

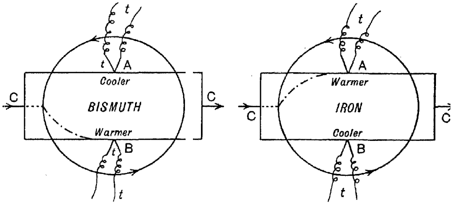

FIG. 51A and B.—Ettingshausen effect.

The change could be reversed both by reversing the current and the direction of the field.

If $\frac{\Delta T}{b}$ is the transverse change in temperature per unit width, the following relationships were found to hold:

$$\frac{\Delta T}{\cdot} = \mathrm{PH}i$$

where H = the strength of the magnetic field,
i = the density of the primary current C,
b = width of the plate,
P = a constant called the Ettingshausen coefficient.

But $$i=\frac{C}{bd}$$

where d represents the thickness of the plate;

hence $$\Delta T=\frac{PHC}{d}$$

In this experiment the approximate dimensions of the plate were as follows: length 3·1 cm., width 2·4 cm. and thickness about 0·04 cm. It is conventional to call the effect positive and give it a plus sign if, in going from the point of the entry of the current C to the warmer point B, the passage CB is in the direction of the current used to excite the field H. If the passage to the warmer point B is opposite to the direction of the current, the effect bears a negative sign. The effect is positive with bismuth and negative with iron.

A large number of theories have been put forward to explain the effect, but none of them hold rigidly. The most notable of these are Riecke's theory[36], Zahn's theory[37] and Livens' theory[38], and Hall also proposed a possible explanation of the Ettingshausen effect and its change of sign. It is easy to conceive that the Hall and the Ettingshausen effects must be related. Zahn and Drude[39] obtained the following relation between the two effects:

$$\frac{R}{P}=0{\cdot}5\times 10^{-2}.p.c\frac{v_1-v_2}{v_1+v_2}$$

where R is the Hall coefficient, P the Ettingshausen coefficient and p is a constant equal to $1{\cdot}65\times 10^{-4}$, c the velocity of light, and v_1 and v_2 are respectively the velocities of the negative and the positive electrons.

11. CHANGE OF RESISTANCE IN A MAGNETIC FIELD

In 1856 Sir William Thomson[40] discovered that a change in resistance of a conductor was observed when it was placed in a magnetic field. He found that the resistance of iron and nickel increased when they were magnetised longitudinally, while in a transverse field both these metals showed a decrease in their electrical resistance. These observations were soon confirmed by a host of other workers, notably Adams, Tomlinson and Goldhammer.

In 1875 Adams[41] pointed out that the change in resistance

Δr was proportional to the square of the field strength, and Tomlinson[42] later gave the following equation which satisfactorily related the change of resistance in the field in the case of magnetisable substances:

$$\frac{\Delta r}{r} = a\mathrm{H} + b\mathrm{I}$$

where a and b are constants dependent upon the nature of the conductor and I is the intensity of magnetisation.

In 1887 Goldhammer[43], after a series of careful experimental researches, put forward the following equations I and II, which were found to hold for non-magnetic and ferromagnetic metals, respectively :

$$\frac{\Delta r}{} = \mathrm{AH}^2 \quad . \quad . \quad . \quad \text{(I) Non-magnetic metals}$$

where A is a constant; and

$$\frac{\Delta r}{r} = a\mathrm{I}^2 \qquad \text{(II) Ferromagnetic metals}$$

in which a is constant and I^2 the square of the intensity of magnetisation.

The exceptionally large increase in resistance produced in bismuth in a magnetic field has made bismuth spiral an instrument of precision for measurements of field strength. Other non-metals studied were antimony, tellurium, graphite and selenium. Some work of interest has also been done on crystals and minerals.

In general, the electrical resistance of non-magnetic metals shows an increase in both transverse and longitudinal fields. The rate of increase is greater in higher fields, and at lower temperatures is proportional to H^2 and depends in magnitude upon the direction with respect to the crystallographic axis. In ferromagnetic metals there is in general an increase in resistance in a longitudinal field and a decrease in the transverse field.

12. ELECTRICAL RESISTANCE IN STRONG MAGNETIC FIELDS (KAPITZA)

An entirely new outlook to the problem of the changes of electrical conductivity in magnetic field has been given by Kapitza, who has systematically examined some thirty-five elements most thoroughly in fields up to 320,000 gauss over a large range of temperature. The elaborate technique of this investigation has been described by Kapitza[44], and the reader is referred to the original paper for details. As impurities have appreciable and occasionally large influence on the electrical conductivity, the elements examined had to be specially purified. Kapitza's samples had a purity of at least 99·9 per cent. and the temperature range was from 88° K., the temperature of the liquid nitrogen, to 290° K., the room temperature.

The relations between $\frac{\Delta R}{R}$, the relative change in resistance, and H, the magnetic field, were obtained by drawing the $\frac{\Delta R}{R} - H$ curve. It was found that if an asymptote be drawn to the linear part of this curve it intercepts the *x*-axis at a magnetic field point denoted by H_K. This value is known as the *critical field* value. The main conclusions of this investigation may be summed up as follows:

(i) For the weaker magnetic fields (below a certain critical value of H_K) the relative change in resistance is proportional to the square of the field or

$$\frac{\Delta R}{R} = \beta \frac{H^2}{3H_K}, \qquad \text{for } H < H_K$$

where β is a constant. This is identical with the Goldhammer equation previously described.

(ii) In stronger fields, ($H > H_K$), the change in resistance increases linearly with the field, or

$$\frac{\Delta R}{R} = \beta\left(H - H_K + \frac{H_K^2}{3H}\right), \qquad \text{for } H > H_K$$

The critical field varies for different elements between 5 and 250 kilogauss. The physical conditions of a conductor, namely forging and annealing, influence the magnitude of H_K considerably, but β remains practically constant. The special features of the elements examined are briefly as follows:

(i) *Elements Li to Au.*—The changes in the value of $\frac{\Delta R}{R}$ are small, but the values of β diminish from light elements to heavy ones.

(ii) *Elements Be to Hg.*—Even at 193° K., the temperature of liquid CO_2, this group shows a large change of resistance.

(iii) *Elements Al to Th.*—The characteristic feature of this group is the smallest critical field H_K for gallium, which is of the order of 5000 gauss only.

(iv) *Elements As to Ta.*—In this group Bi and Sb are exceptions and show the largest change of resistance in the field. Arsenic follows next.

(v) *Elements Cr to Pt.*—Ferromagnetic substances show a considerable change of resistance in weak magnetic fields and comparatively smaller changes in strong fields. The effect amongst members of the eighth group is very small, but elements of the sixth group, Cr, Mo, W, exhibit large changes of resistance in the magnetic field.

Kapitza has put forward a very suggestive theory based on the view that the linear law (ii) rather than the square law (i) is the true law of change of resistance, but owing to initial disturbances in the metal arising out of the internal field distributed at random in the conductor, this is masked when small external fields, less than the critical field H_K, are applied.

The internal field H_i need not be magnetic in origin, although in effect it will be identical with a magnetic field and is in all probabilities a result of the quantum interchange energy as postulated by Heisenberg in his theory of ferromagnetism. Let $\beta_p H_i$ denote the change in resistance due to the field H_i parallel to the current, and $\beta_n H_i$ that due to a field normal to the current, then for

$$H_i \parallel I \qquad \frac{\Delta R}{R} = \beta_p H_i \quad . \quad . \quad . \quad (1)$$

$$H_i \perp I \qquad \frac{\Delta R}{R} = \beta_n H_i \quad . \quad . \quad . \quad (2)$$

Assuming that the total resistance R observed in a metal is equal to the sum of R_i, an ideal resistance, and ΔR_0, an additional resistance for a field H_i distributed at random, then

$$\frac{\Delta R_0}{R_i} = \tfrac{1}{3}(2\beta_n + \beta_p)H_i \quad . \quad . \quad . \quad (3)$$

and

$$R = R_i + \Delta R_0 \quad . \quad . \quad . \quad (4)$$

When an external field H_e is applied, the resultant effect of the vectorial sum of H_e and H_i must be calculable and will depend upon the relative magnitudes of β_p and β_n. In general, where β_p and β_n have both been measured they have been found to differ, but the general character of the result is the same as that when they are assumed to be equal. This assumption gives a simple limiting case which establishes the main points. Let $\beta_n=\beta_p=\beta_0$, then

$$\frac{\Delta R}{R_i}=\beta_0 H^2/3H_K \quad H<H_K$$

$$\frac{\Delta R}{R_i}=\beta_0(H-H_K+H_K^2/3H) \quad H>H_K \quad . \quad . \quad (5)$$

where H_k has the same meaning as H_i. These equations are identical with those experimentally obtained by Kapitza.

This general theory does not apply to semi-conductors like Ge and Te or to Bi, Sb and As. Meissner and Scheffers[45] have shown that for gold it obeys almost perfectly. The theory of Kapitza has opened up a new line of thought and should provide a great stimulus to further investigations in this perplexing field of study.

13. CHANGE OF RESISTANCE IN LIQUID METALS AND ELECTROLYTES WHEN PLACED IN A MAGNETIC FIELD

Drude and Nernst[46] were the first to observe that in a magnetic field of about 8000 gauss the resistance of mercury increased by about 0·2 per cent. Almost double the change was found to take place in molten bismuth at 290°. Des Coudres[47] threw doubt on the observed effect and suggested that the apparent increase may have been due to heat effects of the electric current.

Berndt[48] has supported Des Coudres, while Rossi[49] has brought evidence in favour of Drude and Nernst. It is clear from these facts that the subject is a controversial one and deserves further investigation, particularly now that the technique for obtaining larger magnetic fields has become so highly developed.

A somewhat similar controversy centres round the influence of magnetic fields on the resistance of electrolytes. In 1884 Neesen[50] announced that he observed a diminution in the resistance of a solution of ferrous sulphate placed in a longitudinal field, although no change was observed when a transverse field was applied.

Lussana[51], Hurmuzescu[52] and Milani[53] contradicted these results, although Bagard[54] observed a change of about 1 per cent. in the resistance of a copper sulphate solution in a transverse field of 5000 gauss. In 1907 Berndt[55] again emphasised the negativity of the results in solutions of salts of iron, nickel, cobalt, bismuth and copper. Stifler[56] noted a change in resistance of cobaltous chloride and ferric chloride solutions in a transverse magnetic field of about 20,000 gauss. It was, however, an apparent decrease which was found to be independent of the direction of the field and of the current. In the case of copper sulphate the change in resistance changed sign when the current through the electrolyte was reversed, although it was found to be independent of the direction of the magnetic field. Somewhat similar observations on a large number of substances have been communicated privately by Mata Prasad (1932). Stifler, however, finds the phenomenon to be too complex, and he attributes these changes to causes other than the magnetic field.

Some interesting work on the conductivity of the so-called liquid crystals in magnetic fields has been done by Svedberg[57]. It is well known that when magnetic fields are applied to azoxyanisole, azoxyanisolphenetol and azoxyphenetol a general clearing up of the liquid is brought about. Svedberg noticed that the conductivity of the liquid crystals increased as the length of the molecules was increased. Near the 'clearing point' the effect was found to decrease rapidly and at the clearing point itself the effect vanished altogether. A time factor was also observed. In a field of 200 gauss, 160 seconds were required to reach the maximum effect, while this period was reduced to 90 seconds in a field of 300 gauss.

The influence of magnetic fields on the conductivity of electrolytes is a doubtful phenomenon and has been made complex by a series of contradictory statements. It is a very fascinating subject for investigation, and a deep and accurate study of it will not only clear the subject but will also go a long way in establishing a theory of the change of resistance of a conductor in a magnetic field. Similar anomalous results have been observed in investigations on the influence of magnetic fields on the behaviour of Geissler tubes and other discharge tubes.

14. INFLUENCE OF MAGNETIC FIELDS ON LUMINESCENT BODIES

In a critical investigation, Ives[58] came to the conclusion that in discharge tubes when the field acts on the cathode region only the current flowing through the tube shows an increase. When it acts on the anode region only, it was found to decrease, and when the whole tube was in the magnetic field the current in the tube showed an increase in value. Wilson[59] has also studied the influence of a magnetic field on the conductivity of a flame in a Bunsen burner, and the general effect of the field is to produce an increase in the resistance of the flame.

A number of investigators, notably Malinowski and Lawrow[60], Haber[61], Thornton[62], Lewis[63], Guenault and Wheeler[64], Bernackyj and Retaniw[65], have found that an electrical field influences the temperature of the flame. On analogy the effect deserves to be investigated in a magnetic field.

Recently Dufford, Nightingale and Gaddum[66] have shown that while strong magnetic fields produce no polarisation in the light from the oxy-luminescence of ether solutions of Grignard compounds, they affect its brightness.

An influence of magnetic field on fluorescent gases resulting in considerable decrease of fluorescent intensity has been observed by Steubing[67]. With stronger fields Wood and Dunoyer[68] were nearly able to extinguish the fluorescence. A natural and a very desirable extension of this work will be to investigate the changes in the intensities of phosphorescence of the luminous sulphides in a magnetic field. The results obtained, besides being magnetically important, ought to be of far-reaching importance to the theory of phosphorescence itself.

15. The Nernst Effect

Analogous to the galvanomagnetic effect there are several thermomagnetic effects. For example, the exact analogue of the Hall effect is the development of the transverse thermomagnetic electromotive force first observed by Ettingshausen and Nernst[69] in 1886 and now known as the Nernst effect. The following

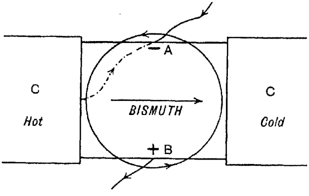

FIG. 52.—Nernst Effect.

arrangement was employed by them in their earliest experiments: A plate of bismuth was held in position by two thick copper clamps, C, C (Fig. 52), one of which was heated while the other was kept cool. A magnetic field H was applied to the plate so that it lay with its plane normal to this field. The edges A and B were connected to a sensitive galvanometer by means of proper heads. When the magnetic field was impressed, the galvanometer indicated a potential difference between A and B, and a current continued to flow from B to A as long as the field was kept on. The direction of the current was changed by changing the direction of the field, or by reversing the flow of heat by making the cold junction hot and the hot junction cold. If the temperatures of the two ends were identical no current was indicated in the galvanometer.

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The Nernst e.m.f. E is given by the following expression:

$$E = Q . H . b\frac{dt}{dl}$$

where Q is the Nernst constant for the metal, b is the width of the plate, H the field strength, and $\frac{dt}{dl}$ the temperature gradient along the plate.

The Righi-Leduc effect [70] and the changes in the Peltier effect in a magnetic field are other examples of the types of phenomena one meets with in this line of work. We have not dealt with them in any detail, as most of these phenomena are interrelated and are analogues of the galvanomagnetic effects. Besides, their theories are imperfectly understood and their bearing on chemical topics is rather remote.

16. THE BARKHAUSEN EFFECT

Barkhausen [71] observed that if the terminals of a coil of wire wound round a strip of sheet iron are attached to the input of a valve amplifier, a very feeble e.m.f. is developed in the coil when the iron is slowly magnetised. As the magnetisation is slowly increased one hears in the loud-speaker a sort of murmur or the sound of a sigh, like the release of gas or steam under pressure. This indicates that the process of magnetisation is a discontinuous operation. It is obvious that these discontinuities must yield valuable information regarding the process itself. It is now believed that as the magnetising force is increased the elementary magnets of the iron rearrange their various-sized groups and, in so turning, produce induction currents in the coil. As the frequency and magnitude of these currents are irregular, they give rise to these quaint notes in the loud-speaker. Forrer[72] and Van der Pol[73] while studying the behaviour of nickel and steel respectively, have shown that the currents induced in the coil in this manner are by no means smooth and they give an irregular curve when investigated by means of an oscillograph. The effect has been extensively studied during recent years, notably by Bozorth[74], Williams[75], Gerlach and Lertes[76] and Tyndall[77]. Zschiesche[78] has shown that the Barkhausen effect is intimately connected with the Joule effect. In single crystals of silicon steel the sound of the Barkhausen effect assumes the largest volume when the magnetic field is so high that irregular and abrupt changes are observable in the elongation and contraction of the single crystals.

The Barkhausen effect is assuming great importance, as it is capable of yielding accurate and valuable information regarding the magnetisation process. This effect also promises to be of special value in investigating the nature of changes which chemical impurities bring about in the intrinsic field of a ferromagnetic material.

In connection with the Barkhausen effect it is interesting to recall the experiments of K. T. Compton and Trousdale[79] to investigate the nature of the elementary 'molecular' magnets which tend to become aligned in the direction of magnetisation. If these elementary magnets are the chemical molecules, or other groups of atoms, one might expect magnetisation to alter the atomic arrangements to such an extent that the Laue diffraction pattern would be altered. According to Compton[80], anything which alters the position of the atoms or changes the distribution of the electrons in a crystal must affect the intensity of the reflection of X-rays. Compton and Trousdale's experiments showed that with a magnetite crystal magnetisation has no effect on the position of the Laue spots and no noticeable effect on their intensities.

A. H. Compton and Rognley[81] later tried to detect a possible change in the intensity of X-ray reflection due to magnetisation in a magnetite crystal. A very sensitive balance method consisting of two Bragg spectrometers was employed which was capable of detecting a change in intensity of 1 per cent. even in the fourth order. The magnetite was magnetised to about one-third of saturation, perpendicular to reflecting surface in one experiment, and parallel to the surface in another. No effect due to magnetisation was observed. These results have been further confirmed by Yensen[82], who used higher magnetic fields to ensure saturation. This furnishes evidence in favour of the view that the elementary magnet is a spinning electron.

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CHAPTER XII

MAGNECRYSTALLIC ACTION

J. A. CROWTHER in his book on *The Life and Discoveries of Michael Faraday* (p. 57) makes the following observations:

'The anomalous behaviour of some crystalline specimens of bismuth, the most diamagnetic of all substances, in the magnetic field now unfortunately led Faraday away on a long series of researches on what he calls magnecrystallic action. He hoped to find some relation between magnetism and the forces at play in building up crystal structure, but the effect, though curious and complex, turned out to be of little importance, and one cannot but regret that so much of Faraday's time should have been spent upon them.'

Not even the worst utilitarian point of view justifies this remark of Crowther, for in the next few sentences in his book he seems to have realised that his observations require to be qualified, and we read: 'One idea of great importance, however, emerges from the experiments, that of magnetic permeability, or as Faraday calls it "the conducting power of a magnetic medium for lines of force". This property of the medium, which corresponds closely to specific inductive capacity in electrical phenomena, is of great importance in practical engineering problems and its existence was first recognised by Faraday as a result of these otherwise somewhat barren researches.' Besides this practical outcome of the researches of Faraday on magnecrystallic action, those familiar with the modern tendencies in magnetism seem to think that Faraday could not with the means at his disposal bring to a more successful issue his efforts in that direction at that time. His searching gaze, however, penetrated into the deep things of nature and he saw clearly at that time what is only slowly dawning on us now, the intimate relationship between magnetic properties and crystalline structure.

I. FARADAY'S FIRST VIEWS ABOUT DIAMAGNETISM

Faraday's earliest view[1] was that the diamagnetic effect was the antithesis of the usual magnetic effect. Thus he thought that in a magnetic field the diamagnetic substance developed North and South poles, while the magnetic substance would have developed South and North poles, respectively. Faraday himself was the first also to feel doubts as to the satisfactory nature of his explanation, although his earlier results pointed to an exact antithesis inasmuch as while one was attracted by the magnet the other was found to be repelled. His classification of the substances preceding air and vacuum to be considered as magnetic or above zero, and those succeeding, below zero or diamagnetic, still implied a true antithesis. That these views of Faraday were not firmly established is clear from the following experiment, which had set him thinking:

'A small glass tube filled with a weak solution of the magnetic substance, iron sulphate, sets itself axially between the magnetic poles, but if it is surrounded as it swings by a strong solution of the same substance it sets equatorially. The tube appears to be magnetic as compared to air; but diamagnetic as compared to the strong solution.'

On this analogy it is possible to explain the antithesis between the behaviour of bismuth and iron on the view that bismuth is less magnetic and iron more magnetic than air. Explaining this, Faraday wrote as follows:

'Such a view also would make mere space magnetic, and precisely to the same degree as air and gases. Now though it may very well be, that space, air and gases, have the same general relation to magnetic force, it seems to me a great additional assumption to suppose that they are all absolutely magnetic, and in the midst of a series of bodies, rather than to suppose that they are in a normal or zero state. For the present, therefore, I incline to the former view, and consequently to the opinion that diamagnetics have a specific action antithetically distinct from ordinary magnetic action, and have thus presented us with a magnetic property new to our knowledge' (*Experimental Researches*, Series xxi. No. 2240, December 1845).

2. PLÜCKER'S INVESTIGATIONS

In August 1848 Faraday met Plücker, who a year earlier had tried to find whether crystalline structure exercised any influence on the deportment of crystals in a magnetic field. From his investigations [2] on the behaviour of several crystals he announced the following rules:

(i) When any crystal whatever with an optic axis is brought between the poles of a magnet, the axis is repelled by each of the poles; and if the crystal possesses two axes, each of these is repelled with the same force by the two poles.

(ii) The force which causes this repulsion is independent of the magnetism or diamagnetism of the mass of the crystal; it decreases with the distance more slowly than the magnetic influence exerted by the poles.

These rules, however, did not retain their importance for long. Thus in 1850 Tyndall pointed out that in the case of calcium and iron carbonate crystals, which are isomorphous, these rules break down completely. While calcium carbonate (Iceland spar) follows Plücker's rule and sets its axis equatorially in the magnetic field the iron carbonate sets its axis from pole to pole.

According to Faraday's diary he met Plücker on August 25, 1848, and saw some of his experiments for the first time. Faraday was evidently much struck by this work, for we notice that he started several investigations himself on this subject; and although definite and right conclusions were not drawn by Plücker, both Plücker and Faraday deserve our appreciation for directing the attention of scientific workers to this important field of enquiry.

3. MAGNECRYSTALLIC BODIES

Later, Faraday [3] undertook a further series of researches on the subject and concluded that a paramagnetic substance, when placed in a magnetic field, causes the lines of force to converge into it, while a diamagnetic substance causes the lines to diverge away from it. This would mean that the magnetic flux per unit area would be greater in a paramagnetic conductor and less in a diamagnetic conductor than when there was no such conductor placed in the field.

Applying these ideas to magnecrystallic bodies, a magnecrystallic substance would be one which allows the passage of magnetic force more readily in one direction than another; this direction being called the magnecrystallic axis. Thus a body, placed in a magnetic field, would experience a force corresponding to this difference, urging it into a position such that the magnecrystallic axis coincides with the magnetic axis.

This effect is masked by a variety of other effects which have to be accounted for. Firstly, there is the effect due to general diamagnetism. When the field is very divergent, the orientation of the crystal is mainly determined by this effect. Secondly, there is the magnecrystallic action which becomes effective only when the field is not very divergent. Thirdly, the shape of the crystal also determines the position which it will assume in a divergent field. After accounting for all these influences, the observed facts can be satisfactorily explained on Faraday's conception of lines of force.

4. TYNDALL'S 'POLARITY HYPOTHESIS'

These views, however, did not find support from many of the advocates of the 'polarity hypothesis', notably Tyndall,[4] who, from his observations, concluded that the cleavage plane of a crystal often determines the position which it will assume when suspended in a magnetic field. Diamagnetic substances like magnesium sulphate, zinc sulphate, saltpetre and topaz tended to set with their cleavage planes equatorially to field; while magnetic substances like nickel sulphate, scapolite and beryl set their cleavage planes axially to the field. Tyndall further explained the rule for the setting of crystals on the basis of structure. He suggested that the cleavage plane is 'the line of closest proximity' of the component molecules in a crystal. If the substance be magnetic, the crystal will tend to set with 'the line of closest proximity' along the field; if diamagnetic, across the field. The magnetic force between two poles is inversely proportional to the square of the distance, and it was natural, therefore, to expect that a closer proximity would result in an increased tendency for the iron particles to set along the line joining the opposite poles, and for the bismuth particles to set across it.

Starting from the idea that the application of external pressure would produce proximity resulting in an artificial magnecrystallic action, Tyndall carried out experiments to study the effect of pressure. He found that a bismuth cube after it had been subjected to external pressure set itself at right angles to its former position. The line of compression turned into the equatorial position, though previously it lay parallel to the field.

These experiments of Tyndall, though important otherwise, must be considered to have failed in their intended purpose. The whole idea of 'proximity' itself is very vague. The effect of the presence of a bismuth particle on the lines of force, as compared to that of iron particle, is so minute that it is impossible to detect it by another piece of bismuth howsoever close the two might be brought together.

5. Diamagnetism in Crystalline Media

The conception of Faraday's lines of force provided a much simpler and real picture of the phenomena of diamagnetism and magnecrystallic action than Tyndall's polarity view and served as the basis for the later theories of magnetism. The idea of resistanceless molecular circuits first postulated by Ampère and Weber has been found to be very useful in distinguishing between para- and diamagnetism. The diamagnetism is proportional to the sum of the projected areas of all these circuits on a plane perpendicular to the lines of force. It is, therefore, independent of the existence of, and variations in, the molecular magnetic fields, provided the sum of the projected areas of the circuits remains constant.

TABLE I

Change in Diamagnetic Susceptibility on Melting (Oxley)

Substance	Change in Specific Susceptibility on Melting
Toluene . . .	+5 per cent.
Ortho-xylene . .	+4·8 ,,
Nitrobenzene . .	+13 ,,
Monochlor-benzene .	+5 ,,
Monobrom-benzene .	+5 ,,
Aniline . . .	+5 ,,
Benzyl chloride .	+5 ,,
Benzoyl chloride .	+5 ,,
Benzene . . .	susceptibility increases on either side of the M.P.
Phenyl hydrazine .	−4·7 per cent.
Acetophenone . .	+4·5 ,,
Naphthalene . .	+4·5 ,,
α-Naphthylamine .	+4·5 ,,
α-Bromonaphthalene	+4·5 ,,
Mercury . . .	+14 ,,
p-azoxy-anisol . .	−6 ,,
Benzaldehyde * .	+5 ,,

* On cooling, ordinarily the liquid passes into the gelatinous state and no change in χ is observed. But if the gelatinous state be carefully avoided, a decrease of 5 per cent. can be observed.

Note.—The sign + indicates that the liquid is more diamagnetic than the crystals. Recently Krishnan, Guha and Banerjee[5] have shown that in naphthalene the difference in the value of χ is less than one half of one per cent. in the molten and the crystalline state, indicating that Oxley's work requires to be repeated on single crystals.

But, when the circuits come very close together, as in crystallisation, the sum of the projected areas may decrease. This would, naturally, entail a change in diamagnetic susceptibility. As an example of this may be quoted the results obtained by Oxley[6] on a large number of organic compounds. According to him the susceptibilities in the crystalline and molten states differ by a few per cent. Oxley's results are summarised in the preceding table.

Honda, Owen, and Honda and Ishiwara[7] noticed a similar change in case of elements. For example, in the case of bismuth the value of χ fell from $-1{\cdot}35$ (solid) to $-0{\cdot}08$ in the liquid state; for lead it fell from $-0{\cdot}12$ to $-0{\cdot}08$ and for zinc from $-0{\cdot}157$ to $-0{\cdot}09$, while in the case of germanium it increased from $-0{\cdot}12$ to $-0{\cdot}39$, and for silver from $-0{\cdot}20$ to $-0{\cdot}29$. These changes are always sudden and abrupt at the melting point.

6. MAGNETIC ANISOTROPY IN CRYSTALS

From what has been said above, it is clear that crystals deserve special consideration from the magnetochemical point of view.

A sphere of isotropic material behaves in all directions in the same way, and in a uniform field it may therefore be rightly considered to be at rest in all directions. On the other hand, a sphere of crystal behaves differently in different directions, and in a uniform field it will quite definitely place itself so that the axis of greatest susceptibility lies along the direction of the field. It may also place itself with the axis of least susceptibility in this direction, but it will then be unstable and the least disturbance will restore the first condition. A sphere of crystals has different susceptibilities in different directions and they can be represented as radial vectors all drawn from a common centre, the end-points of which will then define an ellipsoid—the ellipsoid of magnetic induction, resembling in this respect the corresponding moduli of elasticity. The axes of this ellipsoid of magnetic induction are called the axes of principal magnetisation, and the values of χ are called the principal susceptibilities. In crystals having one axis, the surface is an ellipsoid of rotation, and there are only two principal susceptibilities. In regular crystals the surface may even be a sphere and these materials then do not show any anisotropy. In many crystals the ellipsoid is inclined to be more or less spherical, and the anisotropy from the magnetic standpoint is therefore not considerable.

Some of the substances which show marked anisotropy are shown in Table II, where χ represents the values of principal susceptibilities.

TABLE II

VALUES OF $\chi_{\parallel}$ AND $\chi_{\perp}$ FOR CERTAIN CRYSTALS

Substance	$\chi_{\parallel} \times 10^6$	$\chi_{\perp} \times 10^6$	Name of investigator
C (Graphite)	−2·2	−14·2	Honda and Soné[8]
Bi (Bismuth)	−1·046	−1·487	Focke[9]
$FeCO_3$ (Siderite)	84·2	142·6	Foëx[10]
$ZrSiO_4$ (Zircon)	−0·170	−0·732	Voigt and Kinoshita[11]
Naphthalene (Monoclinic)	−1·10	−4·0	Bhagavantam[12]

7. METHODS OF MEASURING MAGNETIC ANISOTROPY

The earliest method of measuring the magnetic anisotropy of a crystal was to locate its principal magnetic axes and to determine the actual susceptibilities along these directions. It was employed by Voigt and Kinoshita,[11] but does not yield accurate results for the differences of susceptibilities. A method employed by Stenger[13] and Konig[14] and considerably developed by Krishnan, Guha and Banerjee[5] for inorganic crystals, depends upon the fact that a crystal suspended by a thin quartz fibre in a magnetic field, besides experiencing a lateral force tending to move it to the weakest or the strongest part of the field depending on whether it is dia- or paramagnetic, is subject to two different couples in a sense to rotate the crystal about the axis of suspension. The couples are (*a*) due to the asymmetry of the shape of the crystal and the non-uniformity of the field, and (*b*) due to the magnetic anisotropy of the crystal tending to set the axis of the greater susceptibility along the field. The couple (*a*) can be eliminated either by taking the crystal in a symmetrical shape such as a sphere, or, as suggested by Krishnan, by using a strictly homogeneous magnetic field, when the crystal in any shape available may be employed. Suppose a crystal is suspended in a uniform magnetic field: let χ_1 and χ_2 be the maximum and minimum values respectively of the gram-molecular susceptibility of the crystal in the plane of oscillation, then the χ_1 axis will tend to set itself along the magnetic field. If the fibre is torsionless in this position and the crystal allowed to oscillate freely, then it can be shown that

$$\chi_1-\chi_2=\frac{T_0^2-T_1^2}{T_1^2}\cdot\frac{C}{H^2}\cdot\frac{M}{m} \quad . \quad . \quad . \quad (1)$$

where T_1 and T_0 are the period of oscillation with and without the field H, C is the torsional constant of the fibre, *m* the mass of the crystal and M its molecular weight. All the quantities on the right-hand side being experimentally determinable, $\chi_1-\chi_2$ can be determined with great accuracy. Thus the magnetic anisotropy of a crystal can be determined by measuring its periods of oscillation in a uniform magnetic field when suspended along different axes and by comparing them with the corresponding periods of oscillation outside the field. The electromagnet employed should have plane-parallel pole-pieces in order to provide a homogeneous field.

8. ANISOTROPY IN SINGLE CRYSTALS

It may not be out of place here to mention some interesting work done on an allied subject by L. C. Jackson.[15] With the object in view of getting some light on the complicated behaviour of powders which may be regarded as agglomerates of crystals orientated at random, he investigated the principal susceptibilities of single crystals of cobalt ammonium sulphate and nickel sulphate heptahydrate. A modified Weiss method was employed in which the maximum couple exerted on a small thin cylinder of the crystal suspended in a homogeneous field was measured.

Nickel sulphate heptahydrate crystallises in the rhombic form and the crystals are elongated in the direction of the *c* axis. It was found that the Curie constant C_M was almost the same for the three magnetic axes and the curves $\frac{1}{\chi}$, T were all similar to the mean curve. The values for θ in the Weiss equation $\chi(T-\theta)=C_M$ were $\theta_1=59{\cdot}9$, $\theta_2=58{\cdot}0$ and $\theta_3=59{\cdot}7$.

In the case of cobalt ammonium sulphate also, the values of C_M were almost the same for the three axes. The values of *p* were 24·9, 24·5, 24·8. Thus it was clearly shown that the Curie constant remains the same in crystals in different directions although the molecular field may vary considerably. This may suggest that the anisotropy of the crystal arises from differences in the value of the inner Weiss field in different directions. Measurements on the magnetic anisotropy of paramagnetic crystals may throw light on the dependence of the Weiss field on crystal structure.

Mention must also be made here of the excellent work which has been carried out in the laboratories of Raman on the magnetic anisotropy of crystalline substances. Krishnan and Raman[16] have worked on the crystals of sodium and potassium nitrates and on calcite. In the following table the principal diamagnetic susceptibilities for these crystals are given:

TABLE III

PRINCIPAL SUSCEPTIBILITIES IN INORGANIC CRYSTALS

Compound	Crystal system	Axis along which susceptibility is measured	Susceptibility per gm. mole. $\times 10^6$	Average Susceptibility per gm. mol. $\times 10^6$
$NaNO_3$.	Trigonal	$\parallel$ trig. axis	29·5	25·9
		$\perp$ trig. axis	24·1	
$CaCO_3$		$\parallel$ trig. axis	40·6	37·8
(calcite) .	Trigonal	$\perp$ trig. axis	36·4	
KNO_3 .	Rhombic	$\parallel$ '*c*' axis	35·6	31·7
		$\parallel$ '*b*' axis	29·7	
		$\parallel$ '*a*' axis	29·9	
$CaCO_3$		$\parallel$ '*c*' axis	44·4	40·8
(aragonite)	Rhombic	$\parallel$ '*b*' axis	38·7	
		$\parallel$ '*a*' axis	39·2	

It is clear from the above table that crystals of sodium and potassium nitrates and calcium carbonate exhibit a marked diamagnetic anisotropy. In the case of the nitrates the susceptibility perpendicular to the plane of NO_3 ion being always greater for directions in the plane, the difference of susceptibility in the two directions is the same for the two crystals, and the CO_3 ion having the same electronic structure as NO_3 ion gives almost the same anisotropy.

Arguing that magnetic double refraction is an effect arising from the molecules being both magnetically and optically anisotropic and that the optical anisotropy can be known from data on light scattering, Raman and Krishnan derive the following expression by means of which the magnetic anisotropy can be evaluated from the known value of the Cotton-Mouton constant

$$C_m = -\frac{(n_0^2 - 1)(n_0^2 + 2)}{30 n_0 \lambda k T} \cdot \frac{A - C}{2A + C} \cdot (C' - A') \quad . \quad . \quad (2)$$

where C_m is the Cotton-Mouton constant, n_0 is the refractive index of the liquid outside the field, k the Boltzmann constant, C′ and A′ are the susceptibilities of the molecule along and perpendicular to the axis respectively, and A and C are the optical moments and λ the wavelength of light employed.

The anisotropy of the nitrates is shown to be due to the NO_3 ion, and its magnitude is of the same order as expected on above consideration from the known value of the magnetic birefringence of nitric acid liquid.

The conclusions of Raman and Krishnan have been corroborated by S. Bhagavantam [17] on naphthalene crystals and on crystals of iodoform, urea, succinic acid, azobenzene, paranitrotoluene and anthracene. It has been shown that as a rule the aliphatics display a feeble anisotropy, whereas the aromatics in general are highly anisotropic. The magnetic and the optical anisotropy of the benzene ring is shown to be due to the carbon atom in the ring possessing a graphitic rather than the diamond or the tetrahedral structure.

In the interesting investigation of Krishnan, Guha and Banerjee,[5] it has been shown that in favourable cases, for example in diphenyl and dibenzyl, it is possible from magnecrystallic measurements to determine the precise orientations of the molecules in the unit cells. Even in complicated cases like stilbene and azobenzene, when it is not possible to obtain a unique solution, the magnetic data throw considerable light on the question, making it obvious that no structure proposed by the X-ray methods can be acceptable which cannot satisfactorily explain at the same time the observed magnetic properties of the crystal. A large number of inorganic and organic substances, such as quartz, calcite, aragonite, strontianite, witherite, sodium and potassium nitrates, potassium chlorate, barite, celestite, anhydrite, gypsum, sulphur, naphthalene, anthracene, β-naphthol, acenaphthalene, biphenyl, dibenzyl, benzophenone, benzil, azobenzene, hydrazobenzene and salol, have been studied by the above authors. In most cases of organic crystals the mean of the three observed principal susceptibilities agrees well with the value calculated for the substances from Pascal's additivity laws.

In a more recent paper Krishnan, Chakravorty and Banerjee [18] have examined several paramagnetic crystals. Salts of iron and cobalt were found to be strongly anisotropic and the mean susceptibility varied with the nature of the salt, while nickel salts gave only a feeble anisotropy. Several paramagnetic crystals were found to have a large value of χ and small anisotropies, and presented, in consequence, considerable experimental difficulty. A particular case is that of manganese ammonium sulphate, $MnSO_4(NH_4)_2SO_4.6H_2O$, in which for a mean value of gram-molecular susceptibility of $13{,}830 \times 10^{-6}$ the difference between the maximum and minimum principal susceptibilities is found to be only $11{\cdot}4 \times 10^{-6}$, giving an anisotropy of about 0·1 per cent. Jackson and de Haas [19] using single large crystals of this salt had found an anisotropy of over 25 per cent * at the temperature of liquid hydrogen. Since Mn^{++} ion is in ^6S state, theory indicates little or no anisotropy if the ions were really 'free'. Van Vleck,[21] however, gives an upper limit of 1·2 per cent., which can increase about twenty times at 14° K., and Rabi [22] working at room temperature found a value of 0·75 per cent. Jackson and de Haas's value of 25 per cent., in consequence, appeared far too high. In a recent paper Jackson [23] has revised the previous value and considers the anomaly due to internal flaws and crystalline imperfections in the large crystals used by Jackson and de Haas.

The conception of crystalline electric fields as developed by Kramers,[24] Bethe [25] and others [26] has been recently made use of by Van Vleck to explain the anisotropy of crystals. The idea may be expressed thus: that in the case of solids or liquids the effect of the surrounding atoms on a given atom may, to a first approximation, be considered as that of a non-homogeneous external electric field. Considering particularly the case of manganous salts, Van Vleck has derived the following formula to represent the principal susceptibilities:

$$\chi_x = \frac{35N\beta^2}{3k}\left[\frac{1}{T} - \frac{r+s}{T^2} + \ldots\right] \quad . \quad . \quad (3a)$$

$$\chi_y = \frac{35N\beta^2}{3k}\left[\frac{1}{T} - \frac{r-s}{T^2} + \ldots\right] \quad . \quad . \quad (3b)$$

$$\chi_z = \frac{35N\beta^2}{3k}\left[\frac{1}{T} + \frac{2r}{T^2} + \ldots\right] \quad . \quad . \quad (3c)$$

with the assumption that

$$r = \frac{12a+8b}{35k}, \quad s = \frac{4a\sqrt{10}+12e\sqrt{2}}{35k} \quad . \quad . \quad (4)$$

---

* This figure is the value obtained by Krishnan [20] after correcting for a computational error in the original paper.

where β is the Bohr magneton $\frac{eh}{4\pi mc}$ and k the Boltzmann constant.

Where the crystalline field has perfect cubic symmetry the constants a, b, c, d, e are further related as

$$c = e = 0, \quad \text{and} \quad 3a = -2b = \frac{6d}{\sqrt{5}}$$

For the 'mean' or powder susceptibility the relations (3) show that the coefficient of $\frac{1}{T^2}$ vanishes. It is not possible to subject the equation to any rigid test because of the want of reliable data for the individual principal susceptibilities over any sufficiently large range of temperature, more especially at very low temperatures.

Van Vleck emphasises that there is an intimate connection between the anisotropy at room temperature and the amount of deviation of the individual principal susceptibilities from Curie's law, since knowledge of anisotropy at any one temperature permits evaluation of the constants r, s, in equation (3). Further, if the crystalline field has perfect cubic symmetry there is considerable ground for believing that the susceptibility and the paramagnetic part of Verdet's constant would be proportional.

9. THE FERROMAGNETIC CRYSTALS

Besides the effects described above, Weiss [27] and his pupils have shown that ferromagnetic crystals, particularly magnetite Fe_3O_4 and pyrrhotite Fe_7S_8, present a very interesting and complicated field of study. Magnetite shows the property of behaving as a non-isotropic substance. It has a definite crystalline form and belongs to the regular system.

If a thin plate parallel to the cubic surface is cut out of the crystal, then according to the quaternary axes and the cubical symmetry the magnetic properties should repeat themselves four times within 360°, and a curve of the type (1) (Fig. 53) may be expected. It is, however, seen that instead of this curve we obtain different curves of lesser degrees of symmetry according to the intensity of the field. The axes are situated at 0°, 90°, 180°, 270°, and the diagonals of the cubical face pass through 45°, 135°, 225°, 315°. Instead of four waves the first curve obtained with a field of

57·3 gauss shows only two perfect waves 0° to 180° with four null points. The phenomenon repeats itself between 180° and 360°.

Magnetite tends to approach cubical symmetry with increasing magnetic field. The two principal axes of the cubical face are never quite equivalent, and the question arises as to the magnetic behaviour of the third axis. In order to get information on this question, a thin plate parallel to the octahedron has to be cut off the crystal and examined magnetically. This face makes equal angles with all the three axes, although it contains no principal axis. The symmetry can be cubical, quadratic or rhombic;

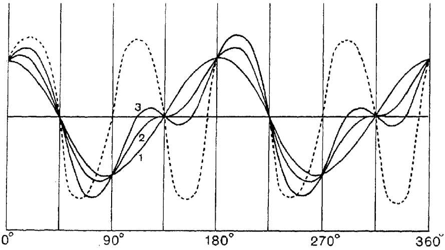

FIG. 53.—(1) H = 57·3 gauss; (2) H = 78·4 gauss; (3) H = 94·5 gauss.

(*a*) If it is cubical within 180°, three equal waves must appear.

(*b*) If the symmetry is rhombic, the three waves, all different, should be possible, and one or two of them may not show themselves at all.

(*c*) If the symmetry is quadratic, two waves should be equal and the third different.

In Fig. 54 it will be seen that when a field of 63·0 gauss is applied only two different waves appear. When the field is increased to 78·7, three waves with different amplitudes make their appearance and they become similar to each other when much stronger fields are applied. If the fields are very weak, only one wave shows itself. From these magnetic properties it is clear that magnetite has the symmetry at least of the rhombic system. A very large number of measurements of the normal and parallel components of magnetisation in thin plates of magnetite in strong and weak fields have revealed the complex character of the phenomenon. According to Quittner,[28] magnetite consists of equal parts of three elements with magnetic planes perpendicular to each other. The molecules are supposed to be arranged so as to form three systems of planes at equal distance from one another. This model magnetite is cut by four systems of intermediate magnetic planes which are parallel to the faces of the octahedron. If all the four planes of cleavage are equal, the crystal presents cubical symmetry; if they are unequal, a lower

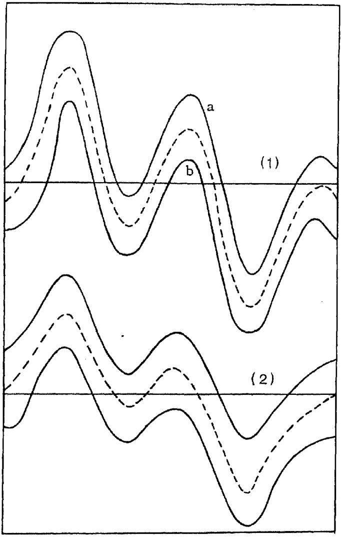

FIG. 54.—(1) H=63·0 gauss; (2) H=78·7 gauss.

degree of symmetry is obtained. Fig. 55 presents such a picture: the upper (*a*) represents a regular and the middle (*b*) an irregular cubic, and the lower (*c*) an irregular octahedral model.

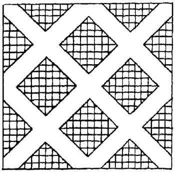

FIG. 55A.—Regular cubic model.

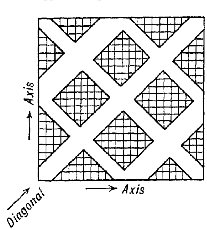

FIG. 55B.—Irregular cubic model.

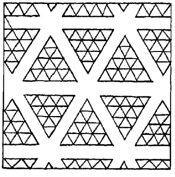

FIG. 55C.—Irregular octahedral model.

The structure of pyrrhotite becomes understandable on the assumption that it is made up of rhombic elements which are parallel to the principal axes and are oriented with the subsidiary axes in three positions lying at 120° to one another. There are abnormal pyrrhotites which are somewhat different in character. From these complicated relationships it appears that the case of amorphous bodies becomes more difficult owing to these so-called isotropic bodies being only quasi-isotropic. In fact, they appear to consist of crystal particles held together at random, and this to some extent manifests itself in their magnetic properties.

10. Single Crystals of Iron and the Influence of Impurities on the Molecular Field

The crystals of iron and haematite have been investigated in a similar manner. It is rather difficult to obtain iron crystals of suitable dimensions. They have, however, recently been prepared by Beck[29] and by Webster,[30] following the method proposed by Freudenreich, which consists in utilising the Goldschmidt process in which the oxide is reduced by aluminium powder. The casting is made in a crucible embodied in sand and slowly cooled down. Beautiful crystals of surfaces up to 2 cm. long are obtained in this way.

Discs of about 4·5 mm. in diameter and 0·35 mm. thick cut parallel to (100) face were employed by Webster, who assumed iron to have a cubical structure. It was found that the saturation intensity was about 1620 for a corrected field of approximately 1000 gauss. Only in the region just below saturation was there some variation in the intensity of magnetisation, and here the maxima along the quaternary axes exceeded the minima along the diagonals by approximately 15 per cent.; and the magnetisation varied with a period of 90°.

The curves for $I_{\parallel}$ and $I_{\perp}$ helped in the evaluation of the resultant intensity I, and from this and the known external field the molecular field could be calculated. The molecular field is a function of the intensity with a proportionality factor, and since iron is believed to be cubical it follows that this factor must be the same for all the different axes. This has brought the extraordinary result that the component of the field was not simply related to the magnetisation along that axis.

It was also found that this molecular field increased to some extent with H. The limiting values of 620 and 470 were obtained for discs from two different crystals. These two different crystals exhibited chemical differences—one was rich in manganese and the other in phosphorus, and further work revealed that the value of the molecular field was considerably influenced by the impurities. This influence of impurities has opened up a new chapter for research work in ferromagnetism, and any satisfactory theory will have to take these extraordinary results into consideration.

11. SUSCEPTIBILITIES AND COLLOIDAL STATE

An interesting offshoot of the main line of investigation has been the study of the magnetic properties of substances in the colloidal state, particularly in the case of bismuth, antimony and graphite. Bismuth in the colloidal form was first investigated by Honda, and by Owen,[31] who found that while the 'regulus' bismuth has a diamagnetic susceptibility of the order $1{\cdot}34\times10^{-6}$, the colloidal bismuth has a value of $0{\cdot}495\times10^{-6}$ only. Vaidyanathan[32] has recently obtained results in the case of graphite, bismuth and antimony which are analogous to those of Honda and Owen. Vaidyanathan was led to these researches by the experiments of Asahara [33] on the X-ray crystal structure of graphite and colloidal graphite. This investigator observed that when graphite was colloidalised for a number of days and the fine particles were investigated, there was no powder pattern, but only a broad diffuse ring such as liquids give near their critical temperature. If the anomalous diamagnetism of bismuth, antimony and graphite is due to crystal structure, then a change in χ should be observed on colloidalisation. Vaidyanathan found that on colloidalisation the susceptibility of graphite powder varied between $-5{\cdot}12\times10^{-6}$ to nearly -2×10^{-6}, and samples showing spongy mass became actually paramagnetic. Bismuth showed a variation of χ from $-1{\cdot}17\times10^{-6}$ to $-0{\cdot}286\times10^{-6}$, and antimony a variation of χ from $-0{\cdot}779$ to $-0{\cdot}535\times10^{-6}$ on colloidalisation.

The experiments of Vaidyanathan are affected by the fact that he did not repeat them in vacuum, even though as he suggests himself, particularly in the case of spongy graphite and bismuth powder prepared by arcing under water, that adsorbed oxygen and oxide formation may be responsible for the low values obtained. Recently the case of bismuth and antimony has been examined by Bhatnagar,[34] and by R. N. Mathur and Varma,[35] and it has been shown that colloidal bismuth obtained by mechanical grinding or by arcing contains sufficient quantities of oxides. BiO_2 and BiO are both paramagnetic as they are odd molecules, and the presence of even traces of these oxides can explain some of the low values which Vaidyanathan has obtained. As a matter of fact colloidal bismuth, after it had been washed with hot tartaric acid solution which dissolves the oxides of bismuth, has been shown to exhibit a diamagnetic susceptibility which is only slightly less than that of 'regulus' bismuth. Incidentally it is interesting to point out that the work of Neusser,[36] which is supposed to show that the sub-oxide of bismuth is not formed, is evidently a misinterpretation of his own results. Neusser determined the specific susceptibility of the so-called sub-oxide and obtained for it a value of $-0{\cdot}39\times10^{-6}$, for the sesqui-oxide of bismuth his value was $-0{\cdot}150\times10^{-6}$ and for bismuth $-0{\cdot}935\times10^{-6}$. Neusser argued that the sub-oxide of bismuth could very well be a mixture or solid solution of bismuth in the sesqui-oxide, and if this is the case the susceptibility of the sub-oxide will be on the line joining the susceptibilities of the metal and sesqui-oxide at the equimolecular composition. The susceptibility for the equimolecular mixture on the values given above lies at $-0{\cdot}393 \times 10^{-6}$, which coincides with that found for the sub-oxide. As it was thought unlikely that it could be a mere coincidence, Neusser argued that the sub-oxide does not exist. Schneider,[37] Muir[38] and several others, however, have established beyond doubt that BiO is formed. If we examine the data of Neusser critically we find that either his experimental values of susceptibilities are totally unreliable as his value of χ for Bi is $-0{\cdot}935 \times 10^{-6}$ against the recognised value $-1{\cdot}37 \times 10^{-6}$, or if his experimental work is correct it is most probable that his bismuth powder already contained a sub-oxide which was much less diamagnetic than bismuth, and the composition examined by him as the sub-oxide was more likely a mixture of bismuth, its sub-oxide and sesqui-oxide.

It is thus evident that the subject of anomalous diamagnetism of bismuth, antimony and graphite requires further examination, and the following possibilities must be excluded before any final conclusion can be drawn:

(i) The presence of adsorbed oxygen and other gases from the atmosphere.

(ii) The formation of the oxides and the sub-oxides during the process of colloidalisation.

(iii) The formation of solid solutions between the metals and the oxides so formed.

As regards bismuth it seems more or less certain that much of the abnormality is due to the formation of the black oxides of bismuth, BiO or BiO_2, or both. A recent support in favour of this view comes from some experiments of Lane[39] in Gerlach's laboratory, who has shown that in films of bismuth in which particle thickness varies from $0{\cdot}2\mu$ to 15μ, no variation of the susceptibility could be found. Lane suggests that the hypothesis suggested by Seemann and Kussmann[40] to explain the effect of cold work on the susceptibility of aluminium and copper alloys, etc. (cf. also Honda), may account for the effect observed in colloidal powders. In the process of grinding as well as cold working slight ferromagnetic impurities in the metals are set free and cause a decrease in diamagnetism.

The researches of Maurain,[41] Kaufmann and Meier[42] and Sorensen[43] on the magnetic properties of thin films of ferromagnetic metals have definitely established that these films behave very differently from metals in bulk. Perhaps the most interesting examples are those of Ingersoll and Vinney,[44] whose sputtered nickel films were devoid of ferromagnetic properties. According to these authors, ferromagnetism appeared after suitable heat treatment, and their first explanation of this phenomenon was that the loss of ferromagnetism was due to the amorphous nature of the film. On heating, the microcrystalline structure returned accompanied by ferromagnetic properties. Ingersoll and Hanawalt[45] have latterly come to the conclusion that in the non-magnetic films of the ferromagnetics, the films are not amorphous as they considered before, but that they show a distension of about 20 per cent. in the lattice spacing. This distension, as they themselves suggest, is due to a chemical or quasi-chemical union of the metal and the gas present.

Recently Rao[46] has confirmed the results of Bhatnagar[34] and Mathur and Varma[35] and has shown that the magnetic susceptibility of bismuth powders of the size about 1μ when washed free of the oxide impurity returns to that of the original material. He, however, finds that the susceptibility value does not completely recover if the metal is powdered to finer dimensions. Working similarly on tin, the atomic susceptibility of which has nearly the value $-41{\cdot}54 \times 10^{-6}$, Rao[47] finds that the susceptibility changes its sign. Dharmatti[48] reports that selenium becomes paramagnetic when powdered to very small dimensions, but this result needs confirmation.

A thorough and careful investigation of the magnetic properties of colloidal metals and anisotropic compounds is bound to lead to further interesting results.

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CHAPTER XIII

THE INFLUENCE OF MAGNETIC FIELDS ON CHEMICAL REACTIONS

THE close relationship between electricity and chemical affinity on the one hand and that between electricity and magnetism on the other early raised the question whether magnetism would alter the character or degree of a chemical reaction. As early as 1881 Remsen[1] observed that magnetism had a remarkable action on the deposition of copper from solution of its salts on an iron plate. In 1886 Nichols[2] further investigated the action of acids on iron in a magnetic field, and in 1887 Rowland and Louis Bell[3] read a paper at the Manchester meeting of the British Association (September 1887) on 'An Explanation of the Action of a Magnet on Chemical Action'. They explained the protection of iron from the chemical action of hydrochloric acid in lines around the edges of the poles by making use of the fact that the force acting on the particle in any direction is proportional to the rate of variation of the square of the magnetic force in that direction. 'This rate of variation is greatest near the edges and points of a magnetic pole and more work will be required to tear away a particle of iron or steel from such an edge or point than from a hollow. This follows whether the tearing away is done mechanically or chemically.'

M. Loeb[4] in 1891 and later Wolff[5] tried the influence of magnetic fields on the oxidation and reduction of iron salts but obtained negative results. Jahr[6] in 1898 observed that a photographic plate immersed in a developer or even in distilled water is effected when brought near the pole of an electromagnet consisting of a bundle of steel wires.

Alexandre de Hemptinne[7] in 1900 published an interesting paper in which he showed that although theoretically there is an effect of the magnetic field, experimentally it is too small to be of much consequence. Among the later workers Berndt,[8] in 1908, found that the rate of solution of iron in hydrochloric acid in a magnetic field is smaller. With zinc no difference was observed. Recently Schukarev[9] performed a series of experiments to detect any possible effect on a number of chemical reactions by subjecting them to transverse and longitudinal magnetic fields ranging from 2000 to 7000 gauss. No general conclusions could be reached by him. Parker and Armes[10] have shown that the reduction of ferric chloride by iron and aluminium and the reduction of permanganate in acid solutions by metallic iron are accelerated by the field. Henglein,[11] however, found no difference in the combination of NO and Cl even with fields up to 20,000 gauss.

1. SOME THEORETICAL CONSIDERATIONS

There are a number of theoretical reasons for expecting an influence of the magnetic field on a chemical reaction involving highly magnetic atoms or molecules. Besides the purely mechanical viewpoint of Rowland we have to take into consideration the thermodynamic aspect of the subject as emphasised by Alexandre de Hemptinne.[7] His main line of argument is that if temperature should have an influence on magnetism the specific heat of the system should also be influenced by magnetic fields. According to Stefan since the magnetism of iron at high temperatures is zero, the specific heat of iron will be greater within the magnetic field than without it. This also points to the possibility of a change in the velocity of reaction involving iron as a participant in the reaction.

Apart from these two particular cases of ferromagnetics, Bhatnagar, K. N. Mathur and R. N. Kapur[12] have considered the general case of chemical reactions on the basis of the law of mass action. If A and B denote the concentrations of the reacting substances and C and D the concentrations of the reaction products, then for the equilibrium state we have

$$\mathrm{A} \times \mathrm{B} \times K_1 = \mathrm{C} \times \mathrm{D} \times K_2$$

or

$$\frac{\mathrm{A} \times \mathrm{B}}{\mathrm{C} \times \mathrm{D}} = \frac{K_2}{K_1} = K$$

where K_1, K_2 and K are the usual constants. For any given concentration the velocities of the forward and backward reactions will then depend upon the constants K_1 and K_2. These constants, while independent of concentrations, vary with the temperature, the medium and other physical conditions.

On the basis of the kinetic theory a molecule (or ion) A collides with another B and either unites to form a third substance C or rebounds elastically. The rate of formation of C will then depend upon the number of inelastic collisions per second between A and B. Any agency, whether internal or external, which affects the probability of inelastic collisions will also affect the rate of reaction between A and B. In a magnetic field the atoms (and ions) assume discrete orientations, that is, they take up certain positions relative to each other. And thus it seems likely that collisions due to molecular agitation will take place in a more orderly and directed manner. This would result in changing the probability of inelastic collisions which in its turn would affect the velocity of the reaction also. This will be considered later in greater detail.

A mechanical analogy of this presents itself when we consider the case of a body possessing inertia, say, a fly-wheel, set into rotation. Such a body will tend to keep up its rotating state. Its motion can be helped by properly directed forces and retarded by opposite ones. If we consider now the case of a paramagnetic substance changing chemically into a more paramagnetic one, and then imagine it to be placed in a magnetic field and regard the field as possessing 'magnetic inertia', the effect of the field should be to so orientate the molecules (or ions) as to facilitate the change. On the other hand, in the case of a substance strongly paramagnetic initially and chemically changing into a less paramagnetic one, the effect of a magnetic field would be to try to 'conserve' the greater paramagnetism of the body and consequently retard the velocity of the reaction. Similarly a chemical transformation from diamagnetic to paramagnetic or less diamagnetic state should be accelerated, and that from a paramagnetic to diamagnetic or from a feebly diamagnetic to more strongly diamagnetic state should be retarded.

Again, considering a reacting system, it is evident that if one of the reaction products possesses a different magnetic state from the rest, it would tend to localise itself in certain parts of the field and to withdraw itself from other parts. The reaction velocity $A \rightarrow B$ will then also vary accordingly. Following similar considerations, J. J. Weigle[13] has obtained a mathematical relation between the concentrations inside and outside the magnetic fields.

A critical study of the previous work on the subject was made by Bhatnagar, K. N. Mathur and Kapur,[12] who showed that in almost all cases where negative results were obtained the reasons could be ascribed to the one or the other of the following causes:

(i) The reactions studied proceeded with great velocity, e.g. the oxidation of ferrous salts.

(ii) The analytical methods employed were incapable of measuring small changes in the amounts of the reaction products.

(iii) There was no appreciable difference between the susceptibilities of the initial substances and the final reaction products.

2. EXPERIMENTAL RESULTS

In view of the contradictory nature of the results reported in literature, Bhatnagar, Mathur and Kapur carried out critical experiments on the following reactions within and without the magnetic field.

I. Reduction of ferric chloride solution containing hydrochloric acid by metallic iron, aluminium and zinc.

II. Dissolution of the metals: iron, aluminium and zinc in dilute hydrochloric acid.

III. Oxidation of oxalic acid by potassium permanganate:

$$2KMnO_4 + 8C_2H_2O_4 = 2MnC_2O_4 + K_2C_2O_4 + 10CO_2 + 8H_2O.$$

IV. Reduction of ferric chloride by hydroxylamine.

V. Reduction of chromic acid by phosphorous acid.

VI. Reduction of chromic acid by organic acids, viz.:

(*a*) by oxalic acid
(*b*) by tartaric acid
(*c*) by lactic acid

VII. Reduction of chromic acid by ammonium oxalate.

VIII. Oxidation of potassium iodide by chromic acid.

IX. Reduction of potassium permanganate by chloral hydrate.

X. The reaction

$$3FeSO_4 + 5KI + KIO_3 + 3H_2O = 3Fe(OH)_2 + 3K_2SO_4 + 3I_2.$$

XI. The reaction

$$3CoSO_4 + 5KI + KIO_3 + 3H_2O = 3CoSO_4 + 3K_2SO_4 + 3I_2.$$

XII. Oxidation of hydroiodic acid by hydrogen peroxide:

$$2HI + H_2O_2 = I_2 + 2H_2O.$$

XIII. Esterification of acetic acid by alcoholic hydrogen chloride.
XIV. Mononitration of phenol.

The results obtained may be summarised as below:

Reaction I.—Reduction of ferric chloride solution containing hydrochloric acid:

(*a*) with iron is accelerated by magnetic field.
(*b*) with aluminium is accelerated by magnetic field.
(*c*) with zinc is retarded by magnetic field.

Reaction II.—Dissolution of metals in dilute hydrochloric acid:

(*a*) The dissolution of zinc is accelerated by magnetic field.
(*b*) The dissolution of iron is retarded by magnetic field.
(*c*) The dissolution of aluminium is not influenced by magnetic field.

Reaction III.—The reaction $2KMnO_4 + 8C_2H_2O_4 = 2MnC_2O_4 + 10CO_2 + 8H_2O$ is accelerated by a magnetic field.

Reaction IV.—Reduction of ferric chloride by hydroxylamine is retarded by a magnetic field.

Reaction V.—Reduction of chromic acid by phosphorous acid is accelerated by a magnetic field.

Reaction VI.—Reduction of chromic acid by organic acids is accelerated by a magnetic field.

Reaction VII.—Reduction of chromic acid by ammonium oxalate is accelerated by a magnetic field.

Reaction VIII.—Oxidation of potassium iodide by chromic acid is accelerated by a magnetic field.

Reaction IX.—Reduction of potassium permanganate by chloral hydrate is accelerated by a magnetic field.

Reaction X.—The reaction $3FeSO_4 + 5KI + KIO_3 + 3H_2O = 3Fe(OH)_2 + 3K_2SO_4 + 3I_2$ is not influenced by a magnetic field.

Reaction XI.—The reaction $3CoSO_4 + 5KI + KIO_3 + 3H_2O = 3Co(OH)_2 + 3K_2SO_4 + 3I_2$ is not influenced by a magnetic field.

Reaction XII.—Oxidation of hydroiodic acid by hydrogen peroxide is not influenced by a magnetic field.

Reaction XIII.—Esterification of acetic acid by alcoholic hydrogen chloride is not influenced by a magnetic field.

Reaction XIV.—Mononitration of phenol is not affected by a magnetic field.

In general for homogeneous reactions it has been found that if $\Sigma_f \chi_M > \Sigma_i \chi_M$, the rate of reaction is accelerated by the field, but when $\Sigma_f\chi_M < \Sigma_i\chi_M$ the rate of reaction is retarded by the field, while with $\Sigma_f\chi_M = \Sigma_i\chi_M$ no change occurs with and without the field.

In the above expressions:

$\Sigma_f\chi_M$ = the sum of the molecular susceptibilities of the final products,

$\Sigma_i\chi_M$ = sum of the molecular susceptibilities of the initial substances.

In the case of heterogeneous reactions it was observed by Bhatnagar, Mathur and Kapur that the rate of solution in hydrochloric acid of iron, which is ferromagnetic, is retarded in the magnetic field, while that of zinc, which is diamagnetic, is accelerated. These results have been confirmed by Rozenberg and Yuza,[14] who have shown that the effect of the magnetic field upon the rate of solution of ferro- and paramagnetic metals in acids is to retard, and in the case of diamagnetic metals to augment the reaction. Similar confirmation is also available from the work of Forestier,[15] who has recently studied the rate of dissolution of iron (99·86 per cent.) in copper chloride solution. He finds that the rate of dissolution in 2 per cent. cuprous chloride solution increases about three times in a magnetic field of about 4500-5000 gauss. He further finds that the rate of solution increases rapidly up to H = approx. 500 gauss, then the increase in the rate is linear up to H = approx. 4500 gauss, after which it remains almost constant.

3. THEORETICAL CONCLUSIONS

We may examine in more detail the rule of homogeneous reactions given by Bhatnagar, K. N. Mathur and Kapur that the velocity of reaction is accelerated, unaffected or retarded by a magnetic field according as

$$\Sigma_f\chi_M \gtreqless \Sigma_i\chi_M$$

There are two possibilities which we may discuss here and which include all those given previously: (i) The tendency for the highly paramagnetic ions to concentrate in the region of the strongest field, and (ii) a change in the probability of the ratio

$$\frac{\text{Number of effective collisions}}{\text{Total number of collisions}}$$

as a result of the discrete orientations postulated by the quantum theory in a magnetic field.

(i) Weigle[13] has shown mathematically that, in the case of a paramagnetic solution placed in a magnetic field, the concentration of the solution within and outside the regions of the strongest field is not the same. In a non-homogeneous field the ions of the solution are subject to a force of attraction or repulsion depending on their para- or diamagnetic moment. For a mixture of liquids Weigle's simplified formula is

$$\frac{n}{n_0} = e^{\frac{\sigma H^2}{2kT}}$$

where n is the concentration where the field $= H$, and n_0 the concentration outside the field.

In a simple solution like nickel sulphate the actual changes in the concentration with and without the field may be almost negligible, due to electrostatic forces, but in a mixture of two salts in which one ion is more highly paramagnetic than the other the ratio of the number of more paramagnetic ions to that of the other may be quite appreciable. Take for example the reduction of chromic acid. Chromium in chromic acid occurs as a complex ion of which the paramagnetic moment is very small. The products of reaction, on the other hand, are highly paramagnetic. Weigle's equation in this case shows that the reaction products should tend to concentrate in the ratio of about 20 : 1 in a field of 2000 gauss. Since the reaction products will be localised in a small area near the poles where H is the strongest, their concentration in the rest of the solution will get lower, and consequently the forward reaction will proceed faster. In the localised region, with the stronger concentration of the reaction product, the back reaction is expected to be stronger, but besides being confined in a smaller region, the amount of the back reaction will be less because of the stronger field in this region, which will quantise the orientations more strongly and thereby conserve the more paramagnetic ions. The resultant of the two effects should be an increase in the forward reaction showing an acceleration of velocity in the field. The reverse will be the case in a reaction in which the reactants have a stronger paramagnetic moment than the reaction products. We have omitted to take into consideration so far the effects of stirring. It is obvious that brisk stirring will equalise the changes of concentration and as such will also equalise the changes in velocity so far as they are due to differences in concentration. This fact has been observed by Parker and Armes and its importance was emphasised by Bhatnagar, Mathur and Kapur. It is likely that much of the discordant results of the previous workers, especially in heterogeneous media, were to be ascribed to an absence of properly controlled stirring. An interesting line of investigation recently undertaken is to map the mechanical location of ferro- or paramagnetic material when a chemical reaction is taking place in a magnetic field by suddenly chilling the solution or fixing the products of reaction in gelatine. This experiment will show how much of the effect is due to mechanical concentration alone.

(ii) We shall now take into account the influence of discrete orientations on the velocity of reaction in a magnetic field.

In a simple gaseous reaction whose velocity is sufficiently slow it is well known that all the molecular collisions do not result in a combination. In fact it is estimated that one collision in about 10^8 may lead to reaction. Considering the large thermal variations of the velocity constant of chemical reactions, McC. Lewis [16] and later Tolman [17] have come to the conclusion that only the exceptional molecules can react and that the exceptional state corresponding to 'activation' is very much favoured by increase of temperature, as the actual number of collisions is increased only slightly.

For a bimolecular reaction in which two molecules enter into collision per second in a unit volume the probability relation

$$\frac{\text{Number of effective collisions}}{\text{Total number of collisions}} = e^{-\frac{E}{kT}}$$

is given by the Maxwell-Boltzmann distribution law. The total number of collisions per second between 'activated' molecules is

$$n = ze^{-\frac{E}{kT}} \quad . \quad . \quad . \quad (1)$$

In order to account for factors such as the form and internal 'phase' conditions of the molecules it is usual to introduce a factor P in the above equation. Thus

$$n = P . z . e^{-\frac{E}{kT}} \quad . \quad . \quad . \quad . \quad (2)$$

According to Hinshelwood [18] the value of P is ordinarily of the order of unity and independent of temperature. The effects of molecular rotation, vibrations and electronic orientations can be allowed for by considering n as

$$n=(n_1+n_2+\ \ldots\ +n_s)=\Sigma_s P . ze^{-\frac{E}{kT}} \quad . \quad . \quad (3)$$

K. N. Mathur[19] has made the assumption that the magnetic field affects the reaction velocity by changing the internal 'phase' condition of the activated colliding paramagnetic molecules.

If, for a paramagnetic ion, $\bar{\mu}$ be the mean effective molecular magnetic moment, then the resultant magnetic moment σ for a gram-molecule in the field direction is $\sigma=N\bar{\mu}$. For a number of different molecules taking part this can be written as $\Sigma_i\sigma$ for the initial and $\Sigma_f\sigma$ for the final products. The difference in the magnetic moments of the initial and final products is $\Sigma_i\sigma-\Sigma_f\sigma$, or since $\chi_M=\frac{\sigma}{H}$ we may write the above expression as $H[\Sigma_i\chi_M-\Sigma_f\chi_M]$.

A 'phase' correction Δ can be introduced in the well-known Arrhenius equation to account for the magnetic field effect, i.e. $\log K=\left(C-\frac{Q}{RT}\right)-\Delta$ where K is the velocity constant and Q is called the 'heat of reaction' and R the gas constant. The equation can then be written as

$$\log K=\left(C-\frac{Q}{RT}\right)-C_1(\Sigma_i\chi_M-\Sigma_f\chi_M)H \quad . \quad . \quad (4)$$

where C_1 is a constant of proportionality.

For a paramagnetic substance, since $\chi_M=\frac{\sigma_0^2}{3RT}$ and σ_0 the saturation magnetic moment is related to p, the Weiss magneton number by the relation

$$p=\frac{\sigma_0}{1123 \cdot 5}$$

equation (4) can be expressed as

$$\log K=C-\frac{Q}{RT}-\frac{C_2}{RT}(\Sigma_i p^2-\Sigma_f p^2)H$$

$$=C-\frac{1}{RT}\{Q+C_2(\Sigma_i p^2-\Sigma_f p^2)H\} \quad . \quad . \quad (5)$$

where $$C_2=\frac{(1123 \cdot 5)^2}{3}C_1=\text{constant}$$

which gives the velocity constant for a paramagnetic reaction.

$\Sigma_i p^2$ and $\Sigma_f p^2$ are the sums of the square of the Weiss magneton numbers of the initial and final products, i.e.

$$\Sigma p^2 = n_1 p_1^2 + n_2 p_2^2 + \ldots$$

The equation (5) satisfies at least in a qualitative manner the requirements of the experimental results. For example, in a reaction in which $\Sigma_f p^2 > \Sigma_i p^2$ the value $(\Sigma_i p^2 - \Sigma_f p^2)$ becomes negative and hence the magnetic factor becomes positive, which would account for the increase in the value of K. The opposite would be the case for $\Sigma_f p^2 < \Sigma_i p^2$. For $\Sigma_f p^2 = \Sigma_i p^2$ the magnetic factor disappears, which is amply confirmed by experimental results.

We have accordingly two factors operating simultaneously—the mechanical factor and the internal 'phase' factor. It is likely that in cases where the solutions are not stirred the mechanical factor may be the more important.

The problem is by no means completely solved, as the experiments on the influence of magnetic fields in gaseous reactions have so far yielded negative results, and in liquid and solid media the theory of internal 'phase' effect may not hold with rigour owing to stronger mutual interaction of the molecules.

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CHAPTER XIV

MISCELLANEOUS USES OF MAGNETIC PROPERTIES IN PHYSICO-CHEMICAL INVESTIGATIONS

THE contribution which the study of magnetic properties of substances has made to our knowledge of atomic and molecular structure has been dealt with in considerable detail in the previous chapters. In this chapter it is proposed to indicate briefly some of the applications of our knowledge of magnetic properties of substances to industry and to chemical investigations other than those on molecular and atomic structure.

1. THERMOMAGNETIC ANALYSIS

A brief account of the profound changes which take place in the physical properties of steel due to chemical impurities and mechanical straining has been given in the chapter on ferromagnetism. These direct uses do not exhaust the technical importance of magnetic measurements. The susceptibility of a metal or an alloy varies with the temperature, and the curve of variation may be used, as thermal curves are used, to study the temperatures of transformation of steels and hence their constitution. This method has been much employed in Japan. Honda and Endo[1] determined the magnetic susceptibility of the iron-carbon system at high temperatures and from the break or discontinuity of the susceptibility concentration curves, the solubility line of cementite, the solidus and liquidus lines and the eutectic horizontal have been drawn.

Honda and Murakami[2] have employed both thermal and magnetic analysis in their study of the iron-silicon system (Fig. 56). They have found that the A_3 point rises with increasing silicon content but the magnitude of the transformation decreases as silicon increases.

Sanford[3] describes an apparatus set up for thermomagnetic analysis. The magnetic effects occurring during cooling or heating a material are studied by an astatic magnetometer and the results give useful information on structural changes or transformations.

2. Magnetic Analysis of the Physical Condition of a Ferromagnetic Material

Reliance has hitherto been placed upon chemical analysis of a small selected piece of steel rod as being representative of bulk. This

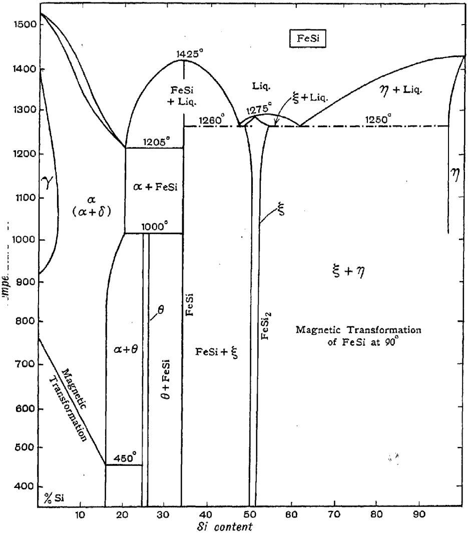


FIG. 56.—Iron-silicon system (Honda and Murakami).

is obviously a poor check, for it may happen that the piece chosen does not represent even 10 per cent. of the bulk. The magnetic analysis aims at providing a method which permits of detecting mechanical flaws or defects in heat treatment without in any way interfering with the structure of the material, and can be applied, for example, in the case of highly polished and finished cutlery blades without producing any blemish on the finished surfaces. The practical importance of this method in testing haulage and winding ropes in mines, testing for flaws in steel rails, rifle-barrel steels, etc., cannot be over-estimated. The method depends on the fact that variations in chemical composition, inhomogeneities in structure, the presence of cracks and internal strains, the processes of mechanical and thermal treatment, etc., all result in variations in magnetic characteristics. The apparatus consists of two coils identically wound and connected in series with the same alternating current flowing through each. A second pair of search coils is placed in each magnetising coil and also connected in series but in opposition. A standard piece of steel, similar in cross-section and specification to those to be tested, is placed in one of the coils, while through the centre of the other coil the rods under test are passed, the feeding being done by a slow-fed motor drive. Both direct and alternating currents are used. Any change in the magnetic homogeneity produces a corresponding change in the flux and so induces an e.m.f. in the search coil. Various types of indicating means are employed, such as galvanometers or oscillographs reflecting a light ray, the latter permitting of photographic recording. Magnetisation by direct current offers advantages where it is desired to make tests at high induction or where the cross-section of the material is large. The alternating current method permits of greater speed in measurements.

Spooner[4] has carried out an extended investigation on high-speed steel which gives much of the information on the subject of testing under alternating current magnetisation. Fischer[5] suggests the possibility of detecting and following the progress of a fatigue crack by magnetic methods. Peltier[6] found that an artificial bubble two mm. in diameter and seven mm. below the surface was faultlessly indicated by a deflection of the galvanometer. Sanford,[7] by employing intense magnetising forces, was able to eliminate the effect due to internal stresses and the flaws in the steel wire ropes became plainly visible.

The record in Fig. 57 (*a*) was obtained with steel wire as used for the manufacture of wire ropes. In Fig. 57 (*b*) is shown the record for the same steel wire as in Fig. 57 (*a*), but in this case the flaws were given intentionally and have been recorded at x, y and z.

Roux[8] has suggested a method of magnetic testing of welded joints. The tests are made by placing the sheet iron to be examined on the square pole-pieces of an electromagnet, covering the sheet iron and strewing iron filings on the paper. When the seam is at right angles to the line of force and free of defects these lines appear continuous. In the case of defective welds the line of welding is marked by an accumulation of filings.

3. MAGNETO-OPTICAL ANALYSIS

Allison and Murphy's magneto-optic method[9] of chemical analysis, depending on investigation of time-lag of the Faraday effect behind the magnetic field as a function of the wavelength of the light used, promises to be of value in quantitative as well as qualitative analysis, and has been treated in detail earlier in Chapter X.

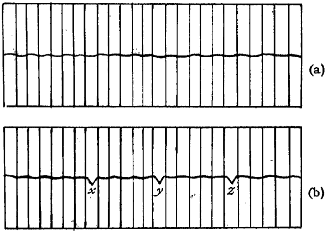


FIG. 57.—Magnetic detection of flaws in steel.

The method has also been employed by Allison and Murphy[10] and by McGhee and Lawrenz[11] in bringing forward evidence for the presence of element eighty-seven in samples of pollucite, lepidolite and samarskite ores. Recently Allison and Bishop,[12] Bishop and Dollins[13] and Goslin and Allison[14] have employed the method in showing that bismuth has fourteen, radium four and uranium, thorium and thallium eight isotopes each.

4. CHEMICAL ANALYSIS AND MAGNETIC SUSCEPTIBILITY

Next to mass, the magnetic susceptibility is perhaps the most additive of all physical properties. The susceptibility-concentration curve is rectilinear for a mechanical mixture and therefore this property can be employed with advantage in determining the proportions of constituents in a heterogeneous mixture of two or more phases. Of the three methods employed in the control of the fractionation of mixtures of the rare earths, viz. the spectral method, the mean equivalent method, and the mean specific susceptibility method, the last one has been found to be the best. The spectral method, while it is unrivalled in proving the purity of the final products, gives only a very approximate idea of the relative proportions of the constituents of a mixture. The mean equivalent method is too tedious and lengthy to be of any great practical use. Stefan Meyer[15] showed that the susceptibility of rare earth oxides varies widely from one member to the other. Urbain and Jantsch[16] showed that the susceptibility is strictly additive in mixtures of rare earth oxides, and from the susceptibility of a mixture the composition of the mixture can be accurately determined. An interesting application of magnetic susceptibility was made by Urbain[17] in his discovery of the element celtium.

G. Singh[18] has found that concentration-susceptibility curves for MnO_2—Mn_3O_4 and NiO—Ni_2O_3 mixtures are linear. This fact is of considerable importance because of its application in the analysis of the oxides. Similar experiments on mixtures of potassium chromate and potassium dichromate seem promising. It is thus seen that magnetic susceptibility determinations could be considerably used in analytical chemistry in estimating substances for which chemical methods are not available.

5. CONSTITUTION OF ALLOYS AND SOLID SOLUTIONS

The general behaviour of the magnetic susceptibilities of alloys of non-ferromagnetic metals has been extensively studied by numerous investigators[19] and very useful information regarding structure, formation of intermetallic compounds, etc., has been elicited from which certain rules have been formulated. In particular, if the alloy consists of a series of heterogeneous mixtures of two phases, then the magnetic susceptibility should vary linearly with the composition by weight from the value of one phase to the value of the other. This is best illustrated by the studies of Honda and Soné[20] and Spencer and John[21] on lead-tin and lead-silver alloys, and of Meara[22] on zinc-antimony series of alloys. The deviations from additivity law reported by Spencer and John[21] in lead-silver alloys have been shown to be due to iron contamination by Montgomery and Ross,[23] who have found that the susceptibility of these alloys varies linearly from the value of lead to that of silver as expected. The formation of intermetallic compounds is indicated by an abrupt change in the slope of the susceptibility concentration curve, e.g. as in the case of Pb-Sb and Te-Sn alloys (Fig. 58).

The investigations on magnetic susceptibility of alloys are thus seen to provide a fruitful method for the detection of compounds in alloys and for the examination of structure of alloys. The importance of this method cannot be over-emphasised as providing additional means of confirming the conclusions drawn from thermal equilibrium diagrams.

While the alloys of almost every metal have been so very extensively investigated, it is surprising to note that no systematic attempt has been made to study the magnetic properties of mercury alloys or amalgams. Recently, investigations have been started in the authors' laboratory in this direction and it has been found that, in the case of copper-mercury alloys, the liquid amalgams having low copper content are merely mechanical mixtures of the two metals and the value of the magnetic susceptibility varies from that of pure mercury to that for pure copper. Another interesting fact noted is a distinct change in susceptibility of amalgams on hardening. This receives confirmation from the observation of Terry and Wright,[24] who have recorded a change in crystal structure of copper amalgams on hardening.

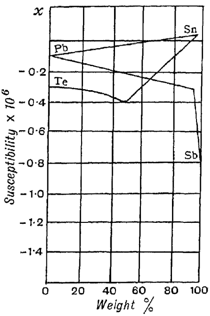


FIG. 58.—Curve for Pb-Sn, Pb-Sb and Sn-Te alloys (Honda and Soné and Endo).

Not only in alloys but also in solid solutions the relationship between magnetic susceptibility and other physical properties is of great significance. Solid solutions of potassium permanganate–potassium perchlorate, potassium chloride–sodium chloride, potassium bromide–potassium chloride and potassium bromide–sodium bromide have been examined by Bhatnagar and P. L. Kapur.[25] In the system potassium perchlorate–potassium permanganate the susceptibility-concentration curve is practically a straight line, while the other systems yield curved graphs. An interesting conclusion is that the greater heat of formation of the solid solution is synonymous with the greater value of the magnetic susceptibility of the system.

6. SUSCEPTIBILITY AND VELOCITY OF CHEMICAL REACTIONS

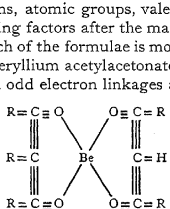
Spencer[26] has suggested the application of magnetic susceptibility measurements to the study of velocity of chemical reactions. As an instance he cites the thermal decomposition of mercurous oxide $Hg_2O = HgO + Hg$. The measurement of the susceptibility can be made on the whole reaction mixture without stopping the reaction or in any way interfering with it, and the composition of the reaction mixture at any moment can be calculated easily.

7. OTHER PHYSICOCHEMICAL APPLICATIONS

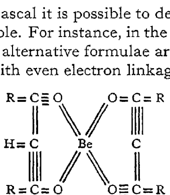
Magnetic susceptibility measurements can also be employed with advantage to test traces of impurities in substances which would be impossible to detect chemically. The composition of cuprous oxide films has been a controversial question for a long time, and only recently Bhatnagar and Mitra[27] have been able to show from magnetochemical data that these films invariably consist of a mixture of Cu_2O and CuO. They have also shown that the reported paramagnetism of Cu_2O is due to its being contaminated with CuO.

Magnetic susceptibility measurements have been employed by Trew and Spencer[28] to determine the association of simple molecules, dissociation of associated liquids, compound formation, etc. Though their results have been contradicted by a number of workers, notably Ranganadham,[29] Buchner[30] and Mathur and Kapur,[31] yet the possibility of this method for detecting such cases remains. Bhatnagar and Lakra[32] have employed this method to show that the molecular state of iodine in various organic solvents is not the same, and that while in nitrobenzene and benzene the dissolved iodine gives a susceptibility value of ionic iodine, in CCl_4 and cyclohexane the value corresponds to that in the solid state.

Angus and Farquharson[33] have employed their investigations on magnetic susceptibility to determine the constitution of beryllium compounds. The proper place for discussing these compounds was in connection with Pascal's work, but as these compounds are believed by Sugden to have a single electron bond which was not known to exist in Pascal's time they have been relegated for discussion to this chapter. By comparing the experimental values with the theoretical ones for the alternative formulae obtained by adding up the susceptibilities for the ions, atoms, atomic groups, valency links and other constitutive correcting factors after the manner of Pascal it is possible to decide which of the formulae is more probable. For instance, in the case of beryllium acetylacetonate the two alternative formulae are (*a*) with odd electron linkages and (*b*) with even electron linkages:

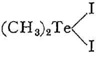


(*a*)



(*b*)

The theoretical value for the diamagnetic susceptibility indicates that the structure is that shown in (*b*).

In some cases it has been found that susceptibility measurements alone cannot offer much information regarding the electronic configuration and chemical constitution of substances unless the variation of the susceptibility with temperature is also studied. For instance, in the case of compounds of the type of tellurium dimethyl dihalides, Sugden[34] has postulated the existence of odd electron linkages to explain their structure. Pauling [35] has shown that a single electron in a bond eigenfunction should have a resultant magnetic moment, and even though the total diamagnetic contribution of the rest of the molecule may mask its paramagnetic effect, the substance ought to show a marked variation with temperature. Further, in a molecule like  $(\mathrm{CH_3})_2\mathrm{Te}\Big\langle{}^{\mathrm{I}}_{\mathrm{I}}$ the single electronic bonds should be at an angle and should have a resultant moment. Bhatnagar and Lahiri [36] have found that the thermal variation of magnetic susceptibility for these compounds is negligible and thus the chances of the presence of single electron bonds in these compounds are greatly reduced. Further confirmation of this view is obtained by comparing the experimental and calculated values of χ after the manner of Angus and Farquharson, and it is seen that the additivity law of Pascal gives the correct values for susceptibility without calling for the aid of correction constants for any bonds other than the simple electron-pair bonds.

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SOME OUTSTANDING PROBLEMS

WHILE the facts of the paramagnetism of the rare-earth and the iron-group ions have received more or less satisfactory explanation from the theoretical standpoint, the same cannot be said, however, about the remaining paramagnetic atoms comprising the palladium, platinum and uranium groups. The atomic structure of these elements resembles that of the iron group. The incomplete shell in each case is the inner *d* shell—4*d* for Pd, 5*d* for Pt and 6*d* for U group—with room for 10 electrons according to the Pauli exclusion principle. The atoms of these elements give wide multiplet separation, and it appears likely on first sight that there should be a good agreement with theory. Contrary to this, however, the agreement between the experimental ionic moments and the theoretically calculated values is entirely absent. As would appear from the table below, the magnetic moments for the ions of many of their compounds have abnormally low values, while some salts of Os, Ir and Pt are actually diamagnetic. The ions Ru^{+++}, Os^{+++} and Ir^{++++} resemble Mn^{++} and Fe^{+++} of the iron group in being in the ^6S state with zero orbital angular momentum, and one would expect them to show a little better agreement with theory. The divergence, as the table shows, is very prominent. The problem is, however, complicated by the fact that these elements enter into salt formation only with difficulty, and for many of the compounds it is not known with certainty whether the paramagnetic ion possesses a simple or complex structure. While the halides, sulphates, etc., of the iron group are definitely known to be simple salts, there is considerable physicochemical evidence to show that in both the Pd and Pt groups the conditions are much more complicated. It is very doubtful whether any of the salts so far magnetically examined were at all simple.

It seems very necessary, therefore, that before any interpretation is possible, an attempt should be made to ascertain the true character of the salts of Pd, Pt and U groups. There appears no reason why the present theories of paramagnetism should not be employed in ascertaining the molecular structure of these groups.

Group	Incomplete Subshell	Ion and Normal Term	Theoretical μ_B		Experimental μ_B
			'Spin only'	$\Delta\nu = \infty$ *	
Pd	$4d^2$	$\mathrm{Mo}^{++++}\ {}^3F_2$	2·83	1·63	0·2 (oxide) *B & Z*
	$4d^3$	$\mathrm{Mo}^{+++}\ {}^4F_{3/2}$	3·87	0·77	3·65† *Bose*
	$4d^4$	$\mathrm{Ru}^{++++}\ {}^5D_0$	4·90	0·0	0·6 (oxide) *G & B*
	$4d^5$	$\mathrm{Ru}^{+++}\ {}^6S$	5·92	5·92	2·1 *Cabrera* 0·3 *Bose* 1·8 *G & B*
	$4d^6$	$\mathrm{Rh}^{+++}\ {}^5D_4$	4·90	6·70	0·4 *Bose and G & B*
	$4d^8$	$\mathrm{Pd}^{++}\ {}^3F_4$	2·83	5·59	0·1 *Cabrera* diam. *Bose*
Pt	..	$\mathrm{Ta}^{5+}\ {}^1S$	0·0	0·0	diam. *Bose*
	$5d^2$	$\mathrm{W}^{++++}\ {}^3F_2$	2·83	1·63	1·8 † ,,
	$5d^3$	$\mathrm{W}^{+++}\ {}^4F_{3/2}$	3·87	0·77	0·4 † ,,
	$5d^5$	$\mathrm{Os}^{+++}\ {}^6S$	5·92	5·92	diam. ,,
		Ir^{++++}	,,	,,	1·9 ,, 0·7 (oxide) *G & B*
	$5d^6$	$\mathrm{Os}^{++}\ {}^5D_4$	4·90	6·70	0·4 *Cabrera*
		Ir^{+++}	,,	,,	0·3 ,, 0·5 † *Bose* diam. *G & B*
		Pt^{++++}	,,	,,	diam. *G & B*
	$5d^8$	$\mathrm{Pt}^{++}\ {}^3F_4$	2·83	5·59	diam. *Bose, Cabrera*
U	..	$\mathrm{Th}^{++++}\ {}^1S$	0·0	0·0	diam.† *Bose*
	$6d^2$	$\mathrm{U}^{++++}\ {}^3F_2$	2·83	1·63	2·4 † ,,

* Van Vleck points out that the departures from '$\Delta\nu$ actual' will not be appreciable for ions other than those in d^4 configuration, for which adequate measurements are not available.

† The salts used were: $K_3MoCl_6 . 12H_2O$, $Mo(SCN)_6(NH_3)_4 . 4H_2O$ for Mo^{+++}, $KTaF_6$ for Ta^{5+}, $K_2W(OH)Cl_5$ and $K_3W_2Cl_9$ for W^{++++} and W^{+++} respectively, $Th(CO_3)_2$ for Th^{++++} and $U(C_2O_4)_2$ for U^{++++}.

NOTE.

(*B & Z*): S. Berkman and H. Zoeller (*Zeits. f. phys. Chem.* **124**, 318, 1927) used MoO_2 for Mo^{++++}.

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(*G & B*): A. N. Guthrie and L. T. Bourland (*Phys. Rev.* **37**, 303, 1931).

The theories of Van Vleck and Pauling have led to remarkable achievements in the interpretation of magnetic behaviour of atoms, ions and molecules. There seems hardly any doubt now that the main problems of magnetochemical investigations in the coming years will be directed towards the extension and application of these theories to facts of molecular magnetism.

The hypothesis of the electron-pair bond which explained the behaviour of molecules so satisfactorily has already found a theoretical justification on the Heitler-London theory and the wave-mechanical principles. The nature and existence of the single and the three-electron bonds are problems which have already begun to engage the attention of investigators in magnetochemistry.

The determination of the susceptibilities of powders and solutions gives only a mean value. The recent refinements in the technique of the measurement of individual susceptibilities along the different axes of single crystals are bound to lead to further interesting developments in the magnetic analysis of crystal structure as furnishing independent evidence supplementing X-ray data. A problem of great theoretical interest is the study of the variation of the constants C and Δ in the Curie-Weiss equation, $\chi = \frac{C}{T - \Delta}$, along the axes of the crystals. Isotropic crystals like those of gadolinium ethyl sulphate * have been found by Jackson and Onnes [1] to follow Curie's law with the same value of C along all the three axes. Anisotropic crystals, on the other hand, may have different values of C or of Δ with the same C along the various axes. There is evidence to show that crystalline anisotropy is directly a function of the distortions introduced by the orbital angular momentum and only indirectly of the spin moments.

The large magnetic and optical anisotropy of the aromatic compounds as compared to the aliphatic series and the difference in behaviour of these two groups with respect to the influence of temperature on magnetic properties are suggestive of an electronic interpretation and await solution. It looks probable that the answer to the question as to why the aromatic substances crystallise more readily than the corresponding aliphatic compounds will also come from magnetochemical considerations.

A problem of considerable interest is the theoretical interpretation of Pascal's corrective constitution constants. Before a definite solution becomes possible somebody will have to take courage in both hands and make accurate measurements of susceptibilities on the large number of compounds examined by Pascal. To anyone who has carefully read Pascal's voluminous work it will be clear that this suffers in the matter of detail and

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* Gd^{+++} ion being in ^8S state has zero orbital angular momentum and in consequence shows no anisotropy.

accuracy in comparison with the more recent magnetic measurements.

As regards purely experimental research, the values of susceptibilities of a large number of compounds described in literature require revision and a number of compounds which are theoretically important have to be investigated magnetically. Another interesting problem is the magnetic study of aluminium in the atomic (gaseous) and the ionic state. In the solid state this element has a feeble paramagnetism which is independent of temperature; its spectroscopic state predicts that it should be highly paramagnetic. Changes in susceptibilities of solutions or polar salts due to the absorption of radiant energy likely to affect the *L-L* couplings have been theoretically postulated but lack experimental verification and present attractive problems.

In spite of the recent developments the whole domain of the ferromagnetic phenomenon is far from clear. While light seems to have dawned on the nature of the molecular field, even such facts as the development of the north, south and the consequent poles in a bar of iron are not clearly explained. While theory attributes ferromagnetism to the spinning electrons, it is not clear as to how an innocent mechanical shock so profoundly alters the magnetic characteristics of ferromagnetic substances. Evidently the interchange interaction theory has to be modified to take the magnetic field of the microcrystalline structure into consideration.

It looks certain that ferromagnetism is not a purely atomic phenomenon like dia- or paramagnetism. It is a 'group phenomenon' or a 'crowd effect' found in molecular state associated with crystalline structure. From all evidence the conviction grows stronger that the small impurities not taken into account by most theories of ferromagnetism may, in association with iron, nickel and cobalt, be the chief cause of the phenomenon itself. It is rather difficult to get rid of infinitesimally small quantities of impurities from the metals, but it would be interesting to see whether the ferromagnetic behaviour becomes less marked with the increasing purity of the specimen. The doubtful purity of the ferromagnetic compounds like manganese bismuthide or manganese boride and the solid-solution nature of these substances lends further support to this view.

A mechanical use of magnetic properties which, though of no immediate use to magnetic theory may yet prove a valuable instrument of research, is the development in the technique of the focussing of beams of electrons by the magnetic and electrostatic lenses first devised by German workers. In its simple form a magnetic lens is a flat (or almost flat) current-bearing coil of wire surrounding an electron discharge tube of the hot cathode type. A converging electrostatic lens may have the form of a metal tube surrounding the electron-emitting cathode and maintained at a suitable negative potential. The electron beam is focussed by electrostatic repulsion as it passes along this tube, and is then made to emerge through a hole in a positively charged plate placed at a short distance from the end of the tube. Important developments may be expected, as theory indicates that for lenses of this type extremely high resolving power may be obtained if aberrations and imperfections could be overcome. An interesting application has been made in a recent experiment described by Bruche.[2] A zinc plate was strongly illuminated by ultra violet light and the photoelectrons ejected were accelerated by a potential difference of 30 K.V. The electrons were next made to pass through a brass tube anode and focussed by a magnetic lens. An enlarged picture of the zinc plate could thus be obtained on a photographic plate. In this way remarkably clear pictures are claimed to have been obtained. In England the technique developed by L. C. Martin and his collaborators attracted much attention at the Physical Society Exhibition in January 1934. 800-volt electrons were passed through a wire gauze or other transmission object, and after focussing with an electrostatic or magnetic lens were projected on to fluorescent screens giving images magnified fifteen times. Von Ardenne[3] has recently described general conditions for the calculation of 'achromatic' electron microscopes. He has calculated a converging system consisting of a magnetic convergent lens with an electrostatic or magnetic divergent lens for 'achromatism'.

Other interesting uses of magnetic properties which have opened up a large field of experimental work and which await further developing, are the recent experiments of de Haas, Wiersma and Kramers[4] on the adiabatic cooling of paramagnetic salts by demagnetisation. A small tube containing CeF_3, surrounded by a vacuum jacket, was hung from the arm of a balance for determining magnetic susceptibility and allowed to dip into liquid He at 1·26° K. A field of 30 kilogauss was applied and the tube itself allowed to cool to 1·26° K. for 4 hours. The field was then abruptly reduced to 2·5 kilogauss and the magnetic moment was measured as a function of time. On extrapolating values of magnetic susceptibility obtained in the normal region of liquid He (4 – 1·3° K.) temperatures lower than 0·18° K. were established to have been attained before the first measurement. The lowest temperatures obtained were 0·13° K. for CeF_3, 0·12° K. for $Dy(EtSO_4)_3.9H_2O$, 0·085° K. for $Ce(EtSO_4)_3.9H_2O$ and 0·05° K. for $KCr(SO_4)_2$.

Interest has recently been revived in the study of what are called liquid crystals.[5] Liquid crystals are neither real crystals nor real liquids. So far most of the knowledge of their structure has been derived from microscopic examinations, which present phenomena of remarkable beauty of colour and pattern. The early work of Friedel had established the existence of two types of liquid crystals distinct from each other—the *smectic* and the *nematic*. Only substances having rod-shaped molecules can form liquid crystals and the smectic and nematic states differ essentially in that, while in the smectic the rod-like molecules are held together in sheets which slide freely over one another, in the nematic state there is no such stratification and the molecules possess a thread-like imbricated arrangement. An example of the former is ethyl-p-azoxybenzoate which is smectic between 114° C. and 120° C., and of the latter p-azoxyanisole which is nematic between 116° and 133° C. The smectics give a simple X-ray diffraction pattern from which it is possible to calculate the actual thickness of the sheets, whereas the nematic state does not give any such simple result. A magnetic field orientates the nematic substances, but has been found to have little effect upon smectic substances owing to the persistence of the layer arrangement. The orientation in nematic substances results in a variation of the optical opacity. Even in a comparatively small field of the order of a few hundred gauss, which is quite insufficient for the orientation of single molecules, the opacity clears up remarkably, as the optic axes assume a common direction. This has been explained by supposing that individual units or 'swarms' of the *micro-liquid-crystalline* are orientated as a whole by the field. The problem is highly interesting from a magnetic point of view and deserves a detailed and careful study.

Since the use of water as a standard substance for measurements of susceptibility ($\chi = -0{\cdot}720 \times 10^{-6}$) has become almost universal, it is interesting to note that H. Auer[6] employing an improved U-tube method has determined the susceptibility of pure water as $\chi = 0{\cdot}72183 \times 10^{-6} \pm 0{\cdot}67$ per cent. and has further confirmed that the temperature coefficient $\frac{1}{\chi_t}\frac{d\chi}{dt}$ falls from $2{\cdot}9 \times 10^{-4}$ at 5° to 0·62 at 70° C. On the other hand, Cabrera and Fahlenbrach[7] give for temperature coefficient a value $+1{\cdot}15 \times 10^{-4}$, constant for all temperatures between 0° and 100° C. The same authors[8] have also investigated the magnetic properties of a sample containing 99 per cent. heavy water in the solid and liquid states, between −60° C. and 150° C. and have compared it with that of normal water. They have found that the diamagnetism of liquid heavy water changes more with temperature and that of solid heavy water less with temperature than that of normal water. They also conclude that at the melting point heavy water is more polymerised.

Amongst the recent contributions on magnetochemical properties of the more uncommon elements may be mentioned the work of P. W. Selwood[9] on the susceptibilities of Sm_2O_3 $5{\cdot}60 \times 10^{-6}$, $SmBr_3$ $2{\cdot}49 \times 10^{-6}$, $Sm_2(SO_4)_3, 8H_2O$ $2{\cdot}34 \times 10^{-6}$. This work has established the existence of $Sm^{\cdot\cdot}$ ions which are identical in electronic configuration with those of $Eu^{\cdot\cdot\cdot}$.

Compounds of Re have been investigated by W. Schüth and W. Klemm.[10] The metallic character of the compounds ReO_3, ReO_2 and ReS_2 is considered to be responsible for the suppression of the ionic paramagnetism, whilst in the trihalides the absence of paramagnetism is attributable to the formation of larger molecules. Compounds of Re^{VII} have been shown to have a very slight paramagnetism which varies with temperature. Further work is clearly indicated on these and other uncommon elements.

A good theory is not unoften a greater incentive to research than a good experiment. An example of this is the recent effort of chemists in exploring and adding organic compounds which are paramagnetic. When the theory of ferromagnetism is fully developed, not only compounds of the type of Heusler's alloys but organic compounds with ferromagnetic properties may perhaps be prepared.

The large magnetic fields obtained by Kapitza and the construction of the Cotton magnet of the Academy of Sciences have brought magnetism to a stage of technical development when a big co-ordinated effort may open up wide vistas of knowledge —not only of magnetism but also of the allied subjects of molecular spectroscopy, dipole moments, X-rays, Raman spectra, etc. The successes of the one will react on the other, and it may be confidently hoped that before long molecular structure will be shorn of its complexity as a result of knowledge gained from the magnetic properties of molecules.

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APPENDIX A

VALUES OF SOME PHYSICAL CONSTANTS

Charge of an electron (e)	$= 4{\cdot}7668 \pm 0{\cdot}0038 \times 10^{-10}$ e.s.u.
	$= 1{\cdot}5900 \pm 0{\cdot}0013 \times 10^{-20}$ e.m.u.
Mass of an electron (m_0)	$= 9{\cdot}038 \times 10^{-28}$ gm.
The Ratio (e/m)	$= 1{\cdot}7592 \pm 0{\cdot}0011 \times 10^{7}$ e.m.u./gm.
Planck quantum of action (h)	$= 6{\cdot}5420 \pm 0{\cdot}0083 \times 10^{-27}$ erg sec.
Boltzmann Constant (k)	$= 1{\cdot}371 \times 10^{-16}$ erg/degree.
Gas Constant (R)	$= 8{\cdot}314 \times 10^{7}$ erg/degree per mole.
Avogadro's Number (N)	$= 6{\cdot}064 \times 10^{23}$ per mole.
Velocity of light (c)	$= 2{\cdot}99796 \times 10^{10}$ cm. per sec.
Number of molecules per c.c. at N.T.P.	$= 2{\cdot}705 \times 10^{19}$.
Volume of one gram-molecule at N.T.P.	$= 22{\cdot}414$ litres.
Bohr Magneton $\left(\beta = \dfrac{eh}{4\pi mc}\right)$	$= 0{\cdot}9174 \times 10^{-20}$ erg per gauss.
	$= 4{\cdot}95$ Weiss Magneton.
Bohr Magneton per gram-molecule (Nβ)	$= 5564$ erg/gauss per mole.
Weiss Magneton per gram-molecule (p)	$= 1123{\cdot}5$ erg/gauss per mole.
Radius of orbit in normal hydrogen	$= 0{\cdot}5284 \times 10^{-8}$ cm.

APPENDIX B

MAGNETIC SUSCEPTIBILITIES OF SOME SUBSTANCES

(20° C., mean values from International Critical Tables)

(*a*) *Common Substances*

	$\chi \times 10^6$
Diamond	−0·49
Graphite	−3·5
Gas carbon	−2·0
Ebonite	0·6
Glass (soda)	approx. −1·0
Quartz	−0·46
Shellac	−0·3
Sulphur	−0·49
Aluminium	0·63
Bismuth	−1·35
Copper	−0·086
Gold	−0·15
Silver	−0·20

(*b*) *Liquids*

Water	−0·720
Mercury 18° C.	−0·19
Oxygen −196° C.	260
Carbon tetrachloride 18° C.	−0·43
Carbon disulphide	−0·54
Alcohol ethyl 18° C.	−0·80
„ methyl 18° C.	−0·74
Glycerine	−0·54
Benzene	−0·71
Sulphur dioxide (liquid)	−0·285

(*c*) *Gases*

(Atmospheric pressure, 20° C.)

Air	24·16
Argon	−0·45
Carbon dioxide	−0·423
Helium	−0·47
Hydrogen	−1·97
Methane	−2·5
Neon	−0·33

(*c*) *Gases—continued*

(Atmospheric pressure, 20° C.)

	$\chi \times 10^6$
Nitrogen	−0·342
Oxygen	106·2
NO	48·66
NO_2	3·26
N_2O	−0·429
NH_3	−1·1

(*d*) *Inorganic Compounds*

H_2SO_4	−0·441
HCl	−0·661
HNO_3	−0·467
P_2O_5	−0·46
As_2O_3	−0·27
As_2S_3	−0·03
Sb_2O_3	−0·19
Bi_2O_3	−0·170
SiO_2	−0·493
TiO_2	0·066
ZrO_2	−0·112
SnO	−0·11
SnO_2	−0·050
PbO	−0·13
Pb_3O_4	−0·24
$Th(NO_3)_4$	−0·14
$InCl_3$	−0·39
TlCl	−0·19
ZnO	−0·362
$ZnSO_4 . 7H_2O$	−0·48
CdO	−0·30
$CdCl_2$	−0·32
HgO	−0·24
$HgCl_2$	−0·19
$CuSO_4$	8·6
$CuSO_4 . 5H_2O$	5·9
AgCl	−0·35
AgI	−0·37
$AuCl_3$	0·43
$PtCl_2$	−0·024
MnO	75·9
MnO_2	38·4
Mn_2O_3	69·0
Mn_3O_4	55·8
$MnSO_4$	88·5
Fe_2O_3	20·6

(*d*) *Inorganic Compounds—continued*

$FeCl_3$	86·2
$FeSO_4$	74·2
$FeSO_4 . 7H_2O$	41·5
$Fe(CO)_5$	−0·40
CoO	74·5
$CoSO_4$	59·6
$CoSO_4 . 7H_2O$	37·0
NiO	53·7 (?)
$NiSO_4$	27·1
$NiSO_4 . 7H_2O$	16·0
$Ni(NO_3)_2 . 6H_2O$	13·6
CrO_3	0·51
$Cr_2(SO_4)_3$	29·5
$Cr_2(SO_4)_3 . 9H_2O$	23·2
MoO_2	0·33
MoO_3	0·88
Mo_2O_3	−0·35
Mo_3O_8	0·30
MoS_3	−0·33
WO_3	0·81
UO_2	7·5
UCl_4	−0·40
V_2O_3	13·9
V_2O_5	0·85
V_2S_3	8·95
V_2S_5	12·6
Cb_2O_5	0·10
$H_4Ta_4O_7$	0·29
B_2O_3	−0·55
Al_2O_3	−0·098
$AlCl_3$	−0·60
$Al_2(SO_4)_3$	−0·48
Sc_2O_3	−0·018
$Sc_2(SO_4)_3$	−0·33
$Sc(NO_3)_3$	0·0
Y_2O_3	0·53
$Y_2(SO_4)_3$	−0·24
La_2O_3	−0·40
$La_2(SO_4)_3$	−0·30
$Ce_2(SO_4)_3$	7·8
Pr_2O_3	15·6
$Pr_2(SO_4)_3$	13·7
Neodymium oxide	29·3
$Nd_2(SO_4)_3$	18·3
Sm_2O_3	6·02

(*d*) *Inorganic Compounds—continued*

	$\chi \times 10^6$
$SmSO_4 . 8H_2O$	2·6
Gd_2O_3	130·1
$Gd_2(SO_4)_3 . 8H_2O$	72·9
Dy_2O_3	229
Er_2O_3	189·1
Yb_2O_3	38
HfO_2	−0·110
BeO	0·0
$BeSO_4 . 4H_2O$	−0·51
MgO	−0·25
$MgSO_4 . 7H_2O$	−0·551
CaO	−0·27
$CaSO_4$	−0·364
SrO	−0·060
$SrSO_4$	−0·315
BaO	−0·13
$BaCl_2$	−0·41
$BaSO_4$	−0·306
Li_2O	−0·57
$Li_2SO_4 . H_2O$	−0·43
$NaBr$	−0·47
$Na_2SO_4 . 10H_2O$	−0·86
KOH	−0·33
KCl	−0·516
K_2SO_4	−0·403
KNO_3	−0·326
$KMnO_4$	0·175
$K_2Cr_2O_7$	0·129
$RbCl$	−0·327
Rb_2SO_4	−0·331
$CsCl$	−0·363
$CsNO_3$	−0·412

(*e*) *Organic Compounds*

		$\chi \times 10^6$
Methyl bromide	CH_3Br	−0·603
Methyl chloride	CH_3Cl	−0·633
Methyl iodide	CH_3I	−0·403
Urea	CH_4N_2O	−0·560
Acetaldehyde	C_2H_4O	−0·502
Acetic acid	$C_2H_4O_2$	−0·526
Ethyl bromide	C_2H_5Br	−0·489
Ethyl iodide	C_2H_5I	−0·679
Dimethyl sulphate	$C_2H_6O_4S$	−0·493
Acetone	C_3H_6O	−0·581

(*e*) *Organic Compounds—continued*

		$\chi \times 10^6$
Propionic acid	$C_3H_6O_2$	−0·587
Ethyl formate	$C_3H_6O_2$	−0·581
Methyl acetate	$C_3H_6O_2$	−0·590
n-Propyl bromide	C_3H_7Br	−0·527
Propyl alcohol	C_3H_8O	−0·766
Succinic anhydride	$C_4H_4O_3$	−0·475
Succinic acid	$C_4H_6O_4$	−0·461
n-Butyric acid	$C_4H_8O_2$	−0·632
n-Butyl alcohol	$C_4H_{10}O$	−0·743
Isobutyl alcohol	$C_4H_{10}O$	−0·798
tert-Butyl alcohol	$C_4H_{10}O$	−0·800
Isobutylamine	$C_4H_{11}N$	−0·843
Pyridine	C_5H_5N	−0·623
Piperidine	$C_5H_{11}N$	−0·755
Amyl nitrate	$C_5H_{11}NO_3$	−0·574
n-Amyl alcohol	$C_5H_{12}O$	−0·766
Isoamyl alcohol	$C_5H_{12}O$	−0·799
tert.-Amyl alcohol	$C_5H_{12}O$	−0·804
Trichlorobenzene	$C_6H_3Cl_3$	−0·587
1, 3, 5-Trinitrobenzene	$C_6H_3N_3O_6$	−0·352
m-Dinitrobenzene	$C_6H_4N_2O_4$	−0·398
2, 4-Dinitrophenol	$C_6H_4N_2O_5$	−0·397
Dinitroresorcinol	$C_6H_4N_2O_6$	−0·312
Bromobenzene	C_6H_5Br	−0·540
Chlorobenzene	C_6H_5Cl	−0·639
Iodobenzene	C_6H_5I	−0·471
Nitrobenzene	$C_6H_5NO_2$	−0·499
Hexane	C_6H_{14}	−0·888
Benzoyl chloride	C_7H_5ClO	−0·539
Benzaldehyde	C_7H_6O	−0·573
Benzoic acid	$C_7H_6ClO_2$	−0·556
Benzyl alcohol	C_7H_8O	−0·705
Anisole	C_7H_8O	−0·672
o-Toluidine	C_7H_9N	−0·701
Anisidine	C_7H_9NO	−0·654
1-Heptine	C_7H_{12}	−0·807
2-Heptine	C_7H_{12}	−0·786
o-Xylene	C_8H_{10}	−0·728
m-Xylene	C_8H_{10}	−0·743
Octylene	C_8H_{16}	−0·798
Octane	C_8H_{18}	−0·872
Octyl alcohol	$C_8H_{18}O$	−0·806
Naphthalene	$C_{10}H_8$	−0·717
Naphthol	$C_{10}H_8O$	−0·673
Camphoric anhydride	$C_{10}H_{14}O_3$	−0·620

(*e*) *Organic Compounds—continued*

		$\chi \times 10^6$.
Camphor	$C_{10}H_{16}O$	−0·680
Citral	$C_{10}H_{16}O$	−0·650
Terpineol	$C_{10}H_{18}O$	−0·725
Diphenyl	$C_{12}H_{10}$	−0·677
Azobenzene	$C_{12}H_{10}N_2$	−0·612
Benzophenone	$C_{13}H_{10}O$	−0·594
Anthracene	$C_{14}H_{10}$	−0·726
Phenanthrene	$C_{14}H_{10}$	−0·718
Oleic acid	$C_{18}H_{34}O_2$	−0·742
Triphenylmethane	$C_{19}H_{16}$	−0·674
Triphenyl carbinol	$C_{19}H_{16}O$	−0·675

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